Phosphorus Dynamics in Stormwater Ponds

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John 4:14

Abstract

Retention ponds are designed to settle particulate phosphorus in the sediments. However, internal loading mechanisms can release bound phosphorus from sediments into the water column, leading to eutrophication conditions in the pond and downstream waterbodies. To understand these mechanisms, twentyone intact sediment and water cores were extracted from four stormwater ponds. Each mesocosm was subjected to different redox conditions and monitored over 30 days. The water column orthophosphate concentrations are used to obtain an overall sediment phosphorus release rate. Phosphorus fractions in the sediment are analyzed to better understand the role of pond sediment characteristics in phosphorus release. Redox sensitive and organic phosphorus concentrations correlated with phosphorus release from the sediments, highlighting the important influence of sediment composition in ponds. These relationships can be used to quantify phosphorus release rates in ponds by fitting regressions to oxygen consumption and sediment P fractions versus the measured phosphorus flux in the mesocosms.

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This research was conducted as part of the Stormwater Research Priorities and Pond Maintenance project through the Minnesota Pollution Control Agency (Objective 3, Task A). The principle investigator is John Gulliver, along with researchers Tyler Olsen, Vinicius Taguchi, and Poornima Natarajan. The methodology was developed by John Gulliver and Tyler Olsen. Field work and laboratory monitoring were led by Tyler Olsen with assistance from Vinicius Taguchi, Peter Corkery, and Poornima Natarajan. Data analysis was performed by Tyler Olsen. Vinicius Taguchi will continue the research for the remaining duration of the project.

Chapter 1

Introduction

Phosphorus has been identified by many as a limiting nutrient in freshwaters, where small amounts of inputs can increase production of algae and bacteria leading to eutrophication (Correll, 1998; Carpenter et al., 1998; Conley et al., 2009). The U.S. Environmental Protection Agency has named phosphorus as one of the primary concerns regarding freshwater quality (U.S.E.P.A., 2017). Phosphorus regulation and mitigation actions have been taken to reduce phosphorus loading to lakes, rivers, streams and ponds. Examples include stricter wastewater treatment discharge permitting, phosphorus ban on fertilizers (MINN. STAT. 18C.60, 2002), and stormwater control measures (SCMs) like swales, buffer strips, sand filters, and stormwater ponds. However, these reductions in external loads are often insufficient because a significant load of phosphorus to waterbodies is released from sediments, labelled internal load. An internal load of phosphorus can occur either under anoxic conditions where redox sensitive phosphorus

is released or with sediment resuspension due to wind mixing or animal disturbance. Internal loading of phosphorus can represent a significant fraction of phosphorus loaded to waterbodies. In Washington state, a study on Lake Sawyer revealed that 18% of the phosphorus load was a result of internal loading (Goodwin, 2017). Similarly, 75% of the phosphorus load to hyper-eutrophic Tucker Lake in Alberta resulted from internal loading (Yonge and Trew, 1989). The phosphorus budget of Half Moon Lake in Eau Claire, Wisconsin, had 42% of the phosphorus come from internal loading (James, 2011). These are some of many examples where internal loading affects lake rehabilitation.

This study focuses on stormwater ponds, instead of lakes. In the State of Minnesota, there are approximately 30,000 stormwater ponds inventoried by researchers at the University of Minnesota (Holmberg, 2016). These ponds are constructed to retain pollutants, primarily phosphorus. The purpose is to understand the dynamics of phosphorus in stormwater retention ponds, specifically conditions that trigger internal release of phosphorus from the accumulated sediments. Because stormwater ponds are part of a larger freshwater network, internal loading of phosphorus can have significant impacts on water quality downstream. Many factors have been found to affect phosphorus release in other water bodies such as dissolved oxygen, temperature, pH, mixing, location within a waterbody, location within a watershed, sediment characteristics, etc. We have synthesized these factors down into four main questions to understand if they also impact ponds:

1. Do dissolved oxygen consumption and concentrations affect phosphorus release

from sediments?

2. Do storm events, and the resulting flush of water from ponds, affect phosphorus release from sediments over time?

3. Does sediment composition affect phosphorus release from sediments?

4. Does location in the pond affect phosphorus release from sediments?

By answering these questions, phosphorus release from pond sediments can be better predicted and used in future applications. First, the relationships discovered in this research can be used to create a model for phosphorus release that can be applied to other ponds. Additionally, this can drive future research designed to predict critical conditions within ponds. Owners and managers of stormwater ponds can also use this research to make maintenance decisions and focus resources on priority ponds that may be releasing high amounts of phosphorus from their sediments that will eventually reach receiving water bodies.

Chapter 2

Review

2.1 Impact of Phosphorus in Surface Waters

Phosphorus has been identified as a critical nutrient in surface waters because it limits primary productivity. When excessive phosphorus is introduced to a water body, it can cause extreme growth of algae, toxic cyanobacterial communities, and cause water turbidity, anoxia, fish kills, and other ecological damages. In heavily developed urban areas, the phosphorus loading to water bodies has been estimated as 1537 kg/yr as compared to phosphorous loading from undeveloped areas (i.e. forests) at 68 kg/yr (Winter and Duthie, 2000). SCMs like ponds, roadside swales, rain gardens, and street sweeping have been implemented in urban settings to reduce the phosphorus load to water bodies. One SCM that helps reduce phosphorus loading to surface waters is stormwater retention ponds, where stormwater is routed through the pond, solids and adsorbed

or bound nutrients settle to the bottom of the pond, and effluent water is directed to receiving water bodies. However, after some time, greater concentrations of phosphorus are being exported than imported. In order to mitigate this, the interaction between water column characteristics and internal loading of phosphorus from the accumulated sediments in the pond needs to be investigated. If the sediments are contributing high quantities of phosphorus to the pond effluent and eventually the receiving water bodies, then maintenance should be performed on the ponds. Indicators for maintenance need and timing are still unknown, but once the relationship between sediment loading and the phosphorus cycle in the pond is better understood, guidelines and standards for maintenance can be developed.

2.2 Factors Influencing Internal Loading of Phosphorus

Phosphorus loading can occur via several different mechanisms including organic matter deposition of leaves, grass clippings, flowers, seeds and other organic sources, adsorption to inorganic compounds, such as metals, clays, silts, carbonates, and biotic uptake (Khalid et al., 1977; Froelich, 1988; Reddy et al., 1995). One explanation for the continued presence of high phosphorus is sediment release of soluble reactive inorganic phosphorus (orthophosphate, PO_4^{3-}) into the water column. Orthophosphate is the most bioavailable form of phosphorus, can travel from the sediment into the water column or vice versa via diffusive processes, and can also bind to metals, such as iron and aluminum, to form solid complexes (Boström et al., 1988).

Oxygen concentration in surface waters has an impact on the rate of internal phosphorus release from sediments, specifically influencing iron cycling. Oxygenated water has the capacity to oxidize available iron to its Fe^{3+} form, which readily binds with orthophosphate. In oxygen deficient waters, these iron complexes are reduced to the free Fe^{2+} form, which no longer chemically binds orthophosphate, and orthophosphate is typically released from solid iron complexes back into the water column. A lake study done by Patrick and Khalid (1974) found that five different sediment types, incubated for 17 days under both aerobic and anaerobic conditions, released more phosphorus during the anaerobic period. Similarly, Wang et al. found that soluble reactive phosphorus release rates were greater in sediments collected in two different lakes under oxygen deficient (<1 mg/L) conditions versus oxygen rich (>1 mg/L) conditions (Wang et al., 2003a,b). An inhibitor to iron binding orthophosphate can be high sulfur. When sulfate is reduced to sulfide, the sulfide permanently binds iron, which reduces the available iron to bind orthophosphate (Caraco et al., 1993).

High temperatures have also been shown to increase release of bound orthophosphate back into the water column. In temperate climates, surface water temperature can fluctuate during the year. Lakes with water temperature that varied between 0.5°C and 20°C showed a positive correlation between temperature and orthophosphate release (Jensen and Andersen, 1992). When water temperature increases, biotic oxygen consumption increases and the oxidized surface layer of the sediment decreases. The resulting anoxic conditions can cause an unfavorable reduction of iron from Fe^{3+} to

Fe^{2+} and an oxidation of orthophosphate, causing a separation of ions that releases the previously bound orthophosphate back into the water column.

Another factor that influences the release of bound phosphorus is pH; as pH approaches a relatively high value, the redox potential increases and orthophosphate is less likely to bind to metals. Wu et al. (2014) and Koski-Vähälä et al. (2001) confirmed that phosphorus release was promoted at pH conditions greater than 9.5 due to ligand exchanges of hydroxide ions with the orthophosphate to bind with metals in the sediments. Although most lakes and ponds have pH values below 9, there are cases where this concern is relevant.

Nitrate and silicate concentrations also have some influence over orthophosphate release into the water column. The iron cycle is often linked with the phosphorus cycle, in that Jensen and Andersen (1992) found that high nitrate inputs ($\sim$4 mg/L) increased phosphorus release rates by stimulating bacterial activity under originally low nitrogen concentrations. They also found that nitrate can depress phosphate release by enhancing the oxidized layer above the sediment. Increased silicate concentrations cause a release of phosphorus due to the competition between silicate and orthophosphate as metal adsorbates in the sediment. However, this process is highly pH dependent, where higher pHs ($>$9.5) allow for more silicate adsorption (Koski-Vähälä et al., 2001).

A final influencing factor on orthophosphate release from the sediment is the movement of gas bubbles from the sediments into the water column. This process is called gas ebullition. Under anoxic conditions, the mineralization of organic matter carbon

performed by organisms causes the creation of methane in the sediments (Martinez and Anderson, 2013). The methane release can cause a disturbance of the sediments, re-suspending organic matter and solutes in the water column. Sediment composition has been shown to influence the rate of methane ebullition. Martinez and Anderson (2013) concluded that silty sediments with intermediate water contents (60-70%) and organic carbon contents (2-3%) had a strong correlation with high gas volume release as opposed to sediments with low organic content and coarse grain sizes. In a flux study where fluoride was injected into sediments and methane was bubbled through the sediments at a constant rate, the fluoride concentration in the water column was 50% higher than in the control setup where fluoride accumulation was due only to diffusive processes (Klein, 2006). Research conclusions on this topic vary, and no unified consensus on the relationship between ebullition and solute diffusion exists.

2.3 Quantification of Sediment-Water Phosphorus Flux

Quantifying internal phosphorus loading in surface waters is important if an understanding of the phosphorus cycle is to be gained. One of the primary methods for quantifying internal phosphorus loading is to set up a mass balance and assume that internal phosphorus load is the portion of the mass balance that cannot be measured. A general mass balance for a lake can be set up as follows:

$$TP = \frac{L_{ext} + L_{int}}{q_s} \times (1 - R_{sed}) \tag{2.1}$$

where TP is total phosphorus concentration (mg/m^3), L_{ext} and L_{int} are the external and internal loads ($mg/m^2/yr$), respectively, q_s is the annual area water load (m/yr), and R_{sed} is the unitless sediment retention of phosphorus defined by $R_{sed} = (L_{ext}\text{-}L_{out})/L_{ext}$ (with L_{out} defined as the load leaving the lake) and can be predicted using lake-specific models or by using theoretical loads (Nürnberg, 2009).

One of the primary laboratory methods for measuring phosphorus flux across the sediment-water interface is using sediment cores and recreating different environmental conditions in a laboratory setting. With the sediment cores, two different courses of action can be taken. The first is that sediment is homogenized in a slurry, water is placed on top of the sediment and water samples are extracted and analyzed for phosphorus content as described by Patrick and Khalid (1974). The second is where the cores that are taken are undisturbed, as to preserve the sediment composition and compaction and set up in column fashion, where water above the sediment surface is sampled and analyzed for phosphorus content (Reddy and Graetz, 1981).

Using sediment homogenization to analyze interstitial water and sediment composition is advantageous for several reasons. First, complicated analyses can be conducted on the material, such as phosphorus extraction and identification using chemical extraction methods (NH_4Cl, NaOH, HCl, etc.) before the cores are established (Boström et al., 1988). This gives a detailed breakdown of the types of phosphorus found in

the sediments, allowing for researchers to make hypotheses on how the phosphorus will interact across the sediment-water interface (Gonsiorczyk et al., 2001). Knowing the sediment composition helps researchers to understand the influence of different types of sediment on phosphorus release. It has been shown that organic and silty sediments are more strongly correlated with phosphorus release compared to clayey sediments with low organic content and higher mineral concentration (Boström et al., 1988). Homogenization also removes the variability of the sediment, phosphorus, and aeration conditions. Replicability of the experiment is easily achieved with homogenization experiments (Wu et al., 2014).

However, when sediment cores are homogenized, the original structure of the sediment core is lost, which can lead to an inaccurate portrayal of the natural dynamics that would occur in the environment. The source-sink relationship with the water column could result in shallow sediments having a different composition than deep sediments. For example, surface sediments that are releasing phosphate to the water column through diffusion would have a lower orthophosphate concentration than deeper sediments. Therefore, phosphate flux from the sediments would be overestimated in the homogenized sediments. In addition, sediment layers can have different phosphorus retention capacities, and depending on the natural sediment hierarchy, the assumed orthophosphate release may be different than naturally occurring orthophosphate release if sediments richer in binding minerals are near the sediment-water interface.

One method to model the natural water column above collected sediment cores is

described by Reddy and Graetz (1981) and replicated by Reddy (1983), where pipes are driven into sediments to collect the core, and the water of interest is added atop the core and allowed to incubate. This process was repeated by Nürnberg (1988), where the cores and overlying water are left undisturbed after collection. From this setup, water samples can be collected from the water column and analyzed for phosphorus. Different aeration conditions can also be modeled using this set up. Other gases can be bubbled in the column to create anaerobic conditions. One disadvantage to this approach is that the scale of each core is small, which makes each column highly susceptible to small changes in the water chemistry. Additionally, if multiple cores are not taken from each site, the phosphorus flux from the lake sediments may be misrepresented due to spatial variation in sediment characteristics.

To enumerate phosphorus release, relationships have been developed to relate lake sediment characteristics and phosphorus release rates. Nürnberg (1988) found that sediment total phosphorus and sediment release rate of orthophosphate are correlated, and linear relationships have been developed for sediment phosphorus mass and release rates using laboratory sediment-water columns. Gonsiorczyk et al. (2001) estimated phosphorus release from lake sediments to follow first-order kinetics, with 81% of the phosphorus released being reductant-soluble, or previously bound to metal hydroxides but released via redox mechanisms. Pettersson (1998) conducted an analysis of two eutrophic lakes, which also showed a positive correlation between sediment total phosphorus concentrations and release rate of orthophosphate.

2.3.1 Phosphorus Flux in Lakes

The most common quantification of phosphorus flux across the sediment-water interface has been applied to lakes. Of these results, those most applicable to stormwater pond phosphorus release are from studies done on shallow, polymictic lakes. Nürnberg (1988) conducted studies on seven lakes and compiled a review of phosphorus release rates in 79 lakes. The range of release rates was from 0 to 51.5 mg/m^2/d, with a mean release rate of 14.1 mg/m^2/d. Another review of Minnesota shallow lakes showed a range of total phosphorus release from 0 to 14.1 mg/m^2/d, with a mean release rate of 6.4 mg/m^2/d (Bassett Creek Watershed Management Commission, 2011). Different environmental factors can influence phosphorus release rates. Generally, higher temperatures and anaerobic conditions increase phosphorus release rates. Out of four lakes studied by Jensen and Andersen (1992), orthophosphate release in whole-lake mass balances was greatest during summer months when temperatures were greatest, and the oxidized layer atop undisturbed sediment cores was thinnest or non-existent. In a study conducted by Larsen et al. (1981), the mean release rate from a small shallow lake (average depth = 5.6 m), calculated from a phosphorus budget was 10.1 mg/m^2/day under anaerobic conditions during the summer months. Wu et al. (2014), in a study of a 2.3 m deep lake, found that the phosphorus release rate from sediments was 3.3 times greater at 30° compared to 20°C, and 4.92 greater under anaerobic conditions as compared to aerobic conditions in sediment batch studies, where dried sediment samples were added to deionized water and subjected to different oxygen concentrations over time. Overall,

release rates from sediments in lakes have positive relationships with oxic conditions and temperature.

Release rates have also been shown to have positive relationships with sediment characteristics. Nürnberg (1988), Pilgrim et al. (2007) and James (2011) developed predictive equations for phosphorus release from lake sediments based on sediment redox sensitive phosphorus concentrations (phosphorus that can be released at low dissolved oxygen concentrations), as listed in Equations 2.2, 2.3 and 2.4. Fe-P is defined as the iron bound phosphorus. Redox-P is defined by the sum of loose-P and Fe-P. Sediment phosphorus concentrations are as mg/g dry sediment, and fluxes are as mg/m^2/day.

$$TP\ Flux = 13.72(FeP) - 0.58 \tag{2.2}$$

$$TP\ Flux = 15.1(redoxP) - 0.7 \tag{2.3}$$

$$Orthophosphate\ Flux = 5.85ln(redoxP) + 13.41 \tag{2.4}$$

Phosphorus fluxes for these models were developed from a study of 17 mesocosms from seven North American lakes for Nürnberg's relation, and 19 mesocosm studies for Pilgrim's relationship. Sediment measurements were made of the top five centimeters of sediment. James' relation is based on a study of a shallow small oxbow lake where

10 sediment cores were taken and converted into mesocosms, and sediment analysis was conducted on the top 4 cm. Nürnberg and Pilgrim's equations are based on total phosphorus release from the sediments, while James' is based on soluble reactive phosphorus (SRP). When flux occurs at the sediments, it is typically as orthophosphate, and then is quickly assimilated by algae in the water column so using either SRP (orthophosphate) flux or TP flux is acceptable for lake applications. Nürnberg and Pilgrim's models use linear regressions (R^2=0.71, 0.90, respectively), and James' model uses a semi-logarithmic regression (R^2=0.68). These three models compare well with each other, predicting similar magnitudes of phosphorus release for a concentration of redox sensitive phosphorus.

2.3.2 Phosphorus Flux in Wetlands and Ponds

Phosphorus cycles have been analyzed in both natural and constructed wetlands and stormwater retention ponds to understand the magnitude and factors influencing release rates. In urban settings, studies have been devoted to monitoring wastewater settling ponds, urban ditches, and other similar SCMs for phosphorus release. Other studies have been dedicated to measuring phosphorus flux from wetlands, both natural and constructed, using mesocosm studies and phosphorus budgets. Wetlands are more typically similar to stormwater ponds than lakes, due to their size and the drainage they receive. Unlike the higher phosphorus release rates from lake sediments, the phosphorus flux from wetland sediments in a study by Hill and Robinson (2012) was measured to be

0.33 to 1.30 mg/m^2/day under anaerobic conditions based on data from 20 cores taken in a 1 m radius at each site. The wetlands in this study received mainly agricultural runoff from nearby fields. An analysis of phosphorus flux from the Florida Everglades wetland sediments resulted in an estimated sediment release rate of 8.31 mg/m^2/day, based off of a mass balance (Reddy et al., 2011). Wetland sediments have a much higher organic content than many lake sediments, which can contribute to high phosphorus release.

Research conducted on phosphorus release from sediments in stormwater ponds is newer, and many conclusions from research on lake sediment phosphorus release have not been researched in ponds. Like wetlands, stormwater ponds are small shallow basins that are capable of releasing phosphorus from deposited sediments over time. While initial stormwater retention of phosphorus may be high (∼45%), the degradation of phosphorus removal capacity increases over time (Adyel et al., 2017; Shukla et al., 2017; Schwartz et al., 2017). During low flow and dry periods in stormwater ponds, influent dissolved phosphorus can be converted to other forms such as particulate phosphorus in the water column, which are exported in higher concentrations. Stormwater ponds can also have a significant organic phosphorus fraction of total phosphorus in the sediment (33-99% P by weight), which can act as a large source of mobile phosphorus when decomposed (Song et al., 2015). In a retention pond that treats mainly agricultural runoff, the phosphorus flux from the sediments to the water column ranged from -1.04 to 0.35 mg/m^2/day, where negative values represent removal of phosphorus from the water column (Reddy, 1983). In Florida, stormwater and agricultural treatment canals were constructed in

2011, and phosphorus fluxes were measured in the water column of laboratory columns comprised of intact sediment cores from the field site and overlying water from the canals. The fluxes were 2.4±1.3, 0.83±0.39, and 0.98±0.38 (±1SD) mg/m^2/day for three different canal locations (Das et al., 2012). The results of these studies indicate that not all ponds have high release. Dynamics in other stormwater ponds may vary from these studies, resulting in higher or lower phosphorus fluxes. Therefore, more research in this area is necessary to understand sediment phosphorus release in urban stormwater retention ponds, and how that affects receiving urban waters.

Chapter 3

Methods

To understand phosphorus cycling in stormwater ponds in both the sediment and water column, laboratory mesocosm studies were conducted using sediment cores and overlying water extracted from stormwater ponds in the Twin Cities metropolitan area. These cores were subjected to different dissolved oxygen (DO) concentrations to simulate the conditions of a stormwater pond. Throughout the treatments, orthophosphate (PO_4^{3-}) was measured in the water column. With these measurements, relationships between phosphorus and key pond characteristics such as dissolved oxygen levels, sediment characteristics, flushing frequency, and location within the pond could be determined and applied to understanding the pond's behavior in varying environments throughout the year.

3.1 Pond Selection

Ponds from several cities in the Twin Cities and greater surrounding area were considered for the study. The cities were contacted for information on their stormwater ponds and asked for ponds that they considered a higher priority and that matched the criteria outlined by the project team. From the responses of each city, a list of approximately 40 ponds was created to examine further. Each of the ponds was visited to determine if they would be good candidates for the study. Grab samples were also taken at each pond using a Nalgene bottle and a PVC extension from the shoreline. These samples were then tested for orthophosphate by filtering the sample through a 0.45 μm membrane filter to remove particulates and using the ascorbic acid colorimetric method, and total phosphorus (TP) on an unfiltered sample using potassium persulfate digestion (Standard Methods 4500-PE; Standard Methods 4500-P B.5; APHA, AWWA, WPCF 1995).

In order to gain a clear picture of phosphorus dynamics in stormwater ponds, several key characteristics were considered before selecting a pond to study. The ponds for the study needed to be more than 10 years old and have little or no dredging maintenance performed on them. This requirement was imposed to examine older ponds that are more likely to release phosphorus. High total phosphorus concentration in the water of the pond (greater than 1 mg/L) indicates that there are significant sources of phosphorus to the pond other than stormwater, which has a typical event mean concentration of 0.10 to 0.20 mg/L (phosphorus, filtered) for most urban settings (Maestre and Pitt,

2005), indicating internal loading as a potential source. Both historical data and grab sample total phosphorus data were used to apply this high total phosphorus criteria and select the final ponds. Accessibility was necessary for the selected ponds to be able to take sediment cores via canoes. Ponds that were not accessible by road or had too much growth surrounding them were not considered.

Following the site visits and grab sample analysis, four ponds were selected for their historical and present high phosphorus concentrations, old age, non-dredged state, good accessibility for sampling, and the cities' cooperation with the study. The ponds are hereby named A, B, C, and D. One exception to these qualifiers is pond C, in which the pond area surrounding the inlet was dredged in 2012. This pond was chosen because its phosphorus concentrations were still high, despite having maintenance performed on it. For more detailed site descriptions for each pond, see Appendix A. Geographical and physical data for the ponds are provided in Table 3.1 and include location, size, approximate mean depth, drainage area, and land use. All of the ponds are located in either residential or commercial (including a school) land use areas. The ponds range in size from 0.04 hectares (pond D) to 0.66 hectares (pond B). The pond mean depths range from 0.6 to 1.8 meters deep. Drainage area to pond size ratios range from 4.26 (pond B) to 106.9 (pond A).

Table 3.1: Physical data for selected ponds

Pond Name	City	Size (ha)	Age (years)	Mean Depth (m)	Drain. Area (ha)	Drain. Area: Pond Area	Land Use
A	St. Cloud	0.21	18	1.8	22.1	105.2	Residential/ School
B	Minnetonka	0.66	>20	1.5	2.8	4.2	Residential
C	Roseville	0.23	>30	1.2	15.4	67.0	Residential
D	Roseville	0.04	>20	0.6	1.8	45	Commercial

3.2 Field Sampling

Sediment quality samples, and intact sediment cores (hereafter referred to as mesocosms) were collected. Field sampling of the mesocosms from each pond was conducted by attaching drive rods to polycarbonate tubes and driving them into the sediment. When the desired length of the sediment in the mesocosm was reached (approximately 30 cm), the top of the polycarbonate tube was capped under the water to create a vacuum in the tube. The rods were then pulled out and the bottom of the tube was capped under water before removing the tube and core completely.

In each pond five mesocosms were taken across the pond, with at least one being taken near the inlet, outlet, and middle of the pond. Detailed maps of sampling locations are given in Appendix A. In pond A, a sixth mesocosm was taken because one had a very sandy sediment, and was not representative of the mucky organic soil that was observed in the rest of the pond. Samples were also collected to assess sediment characteristics following the same method as for the intact cores. These samples were drained of

overlying water and emptied into plastic sealable bags and stored at 4°C for potential analysis.

Dissolved oxygen profiles were also taken at each sampling location. Measurements were taken every 25 cm, starting at the water surface to the approximate bottom of the pond. Temperature and conductivity profiles were taken in the center of each pond, and at some inlet and outlet locations in the ponds. The temperature and conductivity profile data are given in Appendix A.

3.3 Laboratory Monitoring

3.3.1 Mesocosm setup

After sampling, the mesocosms were transported back to the laboratory. Water quality samples from each mesocosm were taken and analyzed for TP and orthophosphate following standard methods (Standard Methods 4500-PE; Standard Methods 4500-P B.5; APHA, AWWA, WPCF 1995). The mesocosms were then drained, and the overlying water was filtered through a 1.2 μm glass fiber filter to remove any particulates. The filtered water was added back into the columns carefully to avoid sediment resuspension. The mesocosms were finally setup for monitoring, which consisted of inserting vinyl tubing with a porous air stone to 8 cm above the sediment surface and capping the top of the polycarbonate tubing. The vinyl tubing was attached to either an aquarium pump or an ultra-pure nitrogen gas cylinder to replicated oxic (>9 mg/L) and anoxic

conditions (<0.3 mg/L) in the mesocosms, respectively. The mesocosms were covered with plastic tarps to prevent light exposure. Laboratory ambient temperature was 20°C for the duration of the experiment. A schematic of the setup is given in Figure 3.1.

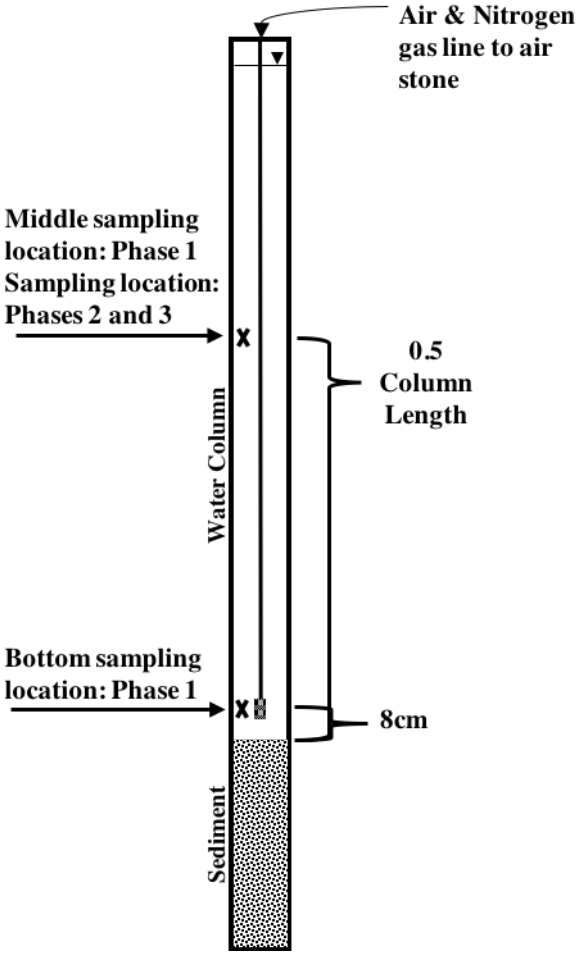

Figure 3.1: A schematic of the mesocosm setup in the laboratory

The laboratory monitoring of the mesocosms was broken up into three phases. A schematic of these phases is given in Figure 3.2. These phases were designed to mimic the conditions that a stormwater pond might experience.

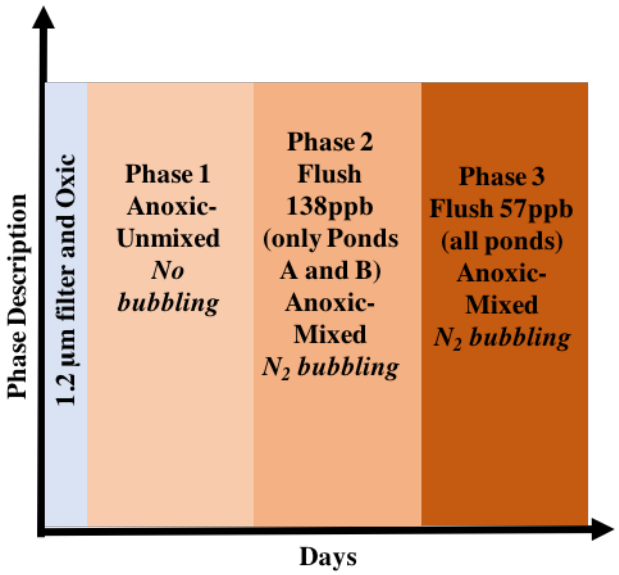

Figure 3.2: Timeline of mesocosm monitoring with descriptions of each phase, where nutrient concentrations are for phosphate in the synthetic stormwater flushes between each phase.

Phase 1 represents a pond that is mixed after a storm event, but remains unmixed for a significant time period afterwards. The first phase began with oxic conditions in the mesocosms, where the entire water column was completely mixed using air bubbled through the water column. After a few days as oxic, the air pump was switched off and the mesocosms were quiescent. The DO was allowed to drop until it was 0.3 mg/L or less, after which it was labeled as the anoxic period.

Phase 2 consisted of flushing the mesocosms with new synthetic stormwater, and bubbling nitrogen to simulate anoxia where the DO is less than 0.3 mg/L at the beginning of the phase and the water column is completely mixed. This occurs in a pond after all of the oxygen has been consumed, specifically just above the sediment. Prior

to flushing, the columns were cleaned. The synthetic stormwater used was based on a similar recipe used by Erickson et al. (2016) which had typical stormwater concentrations of nutrients that are given in Table 3.2. Metals were neglected in the synthetic stormwater because the concentrations are typically low. The nitrate concentrations for each phase were below the threshold where nitrate affects phosphorus release, as reported by Jensen and Andersen (1992). Ponds C and D were not flushed with synthetic stormwater, but rather nitrogen bubbling was turned on directly at the end of the first phase because these columns did not consume all of the dissolved oxygen in Phase 1.

Phase 3 for all ponds consisted of a synthetic stormwater flush, followed by nitrogen bubbling. This phase simulates pond conditions after all of the oxygen has been consumed, specifically just above the sediment. The concentration of the synthetic stormwater for phase 3 was lower than the flush for phase 2 to test how influent P concentrations might affect orthophosphate release from the sediments. The initial water chemistry conditions for the beginning of each phase are given in Table 3.2. Alkalinity and hardness were not measured for the original pond water of phase 1. The initial nitrate concentration for phase 1 is an average of mesocosms from ponds A and B (n=11). The initial phosphate concentration for phase 1 is an average of all mesocosms (n=21).

3.3.2 Sampling and analysis procedures

The concentration of orthophosphate in the water column was monitored over time for approximately 30 days in each phase. Water samples were taken every day or every

Table 3.2: Initial water quality conditions

Nutrient	Phase 1	Phase 2[1]	Phase 3
NO_3-N (ppb)	107[2]	570	570
PO_4^{3-}-P (ppb)	12.3[2]	138	57
Alkalinity (mg/L as $CaCO_3$)	NA	109	150
Hardness (mg/L as $CaCO_3$)	NA	10	40

[1]Ponds C and D were not flushed after Phase 1 because of low release. The initial concentrations for Phase 2 for these ponds are the same as at the end of Phase 1

[2]An average of the individual ponds' water collected from the field

other day during the first week of the phase, and once a week for the rest of the phase.

Water sampling was conducted by drawing approximately 15 mL of water through Tygon tubing attached to an acid-washed syringe. During the first phase, two water samples were taken at 8 cm above the sediment surface and the middle of the water column because the water column was unmixed. During the last two phases, one sample was taken at the middle of the water column because the entire water column was fully mixed via the bubbling of nitrogen.

Water samples were filtered through a 0.45 μm membrane filter to remove particulates, and analyzed for orthophosphate using the ascorbic acid colorimetric method (Standard Methods 4500-PE; APHA, AWWA, WPCF 1995). Additionally, TP measurements were made on select water samples to see if particulate phosphorus was a significant fraction in the mesocosms. Unfiltered water samples were processed according to standard methods (Standard Methods 4500-P B.5; APHA, AWWA, WPCF 1995). Initial pond water from the ponds was analyzed for nitrate using 0.45 μm filtered water samples in a Metrohm 930 Compact IC Flex ion chromatography using 3.2 mM sodium carbonate - 1 mM bicarbonate eluent.

Measurements of dissolved oxygen (DO) and temperature (T) were taken in the mesocosms using a YSI ProDO optical probe, calibrated using the saturated air method. pH measurements were taken using a Jenco model-69 digital pH meter and probe calibrated with pH 4.01 and 7.01 standards. Dissolved oxygen, temperature, and pH measurements were taken by lowering the respective probes down the water column slowly to minimize mixing along the water column. For the first phase, measurements were taken every 15 cm, starting at 8 cm off the sediment surface. During the completely mixed anoxic phases, one DO measurement was taken at the middle of the water column.

3.4 Sediment Extrusion and Analysis

Post-experiment mesocosm sediment samples were extruded for phosphorus analysis in 1 cm increments up to 5 cm, and 3 cm increments from 5 to 11 cm below the sediment water interface. All mesocosms from pond A, and the mesocosms B3, B4, B5, C1, C2, C3, D2, D4, and D5 were analyzed for sediment phosphorus fractions. The layers of sediment were then homogenized by massaging the samples in a plastic bag for 2 to 5 minutes. Method tests showed that the homogenization for 2 minutes was accurate to approximately 5% of the 5-minute tests. Two 3 to 10 g subsamples were taken from the homogenized sediment layers: one for the phosphorus extraction procedure and one for water content (100°C) and loss on ignition (550°C). The moisture content was used to convert wet sediment weights to dry sediment weights for P fractions in the sediment,

and the loss on ignition gives the organic matter content of the sediments.

Sequential phosphorus extractions were conducted on a subsample from the sediment layers using a method of Engstrom (2010) based on methods by Hjieltjes and Lijklema (1980), Psenner and Puckso (1988) and Kopácek et al. (2005). The sequential extraction procedure measures loosely-bound and $CaCO_3$ bound P (loose-P), iron bound P (Fe-P), aluminum bound P (Al-P), mineral-bound P (mineral-P), labile organic P (labile-P), and residual organic P (residual-P) on wet sediments. Loose-P was extracted using 1 M NH_4Cl reagent. Fe-P was extracted using 0.11 M $NaHCO_3$ - 0.1 M $Na_2S_2O_4$ reagent and preserved with 2.0 N HCl. Al-P and labile-P were extracted in a two-step process. First, the sediment was digested using 0.1 M NaOH reagent. Then, with the NaOH digested extract, aluminum phosphorus was extracted using 0.16 M persulfate reagent and 11 N sulfuric acid. The difference between the NaOH and persulfate extractions gave the labile-P concentration. Mineral-P was extracted using 2.0 N HCl reagent. Residual-P and total phosphorus (TP) determination were digested with 30% H_2O_2 and 2.0 N HCl, and preserved with 1.0 M $Na_2S_2O_5$. A comparison of the digested TP concentration and the sum of all fractions TP concentration revealed that the average percent difference between the measurements was 14%, where the digested TP measurement is higher than the sum of the TP. Between each extraction step, the sediment and extracts are separated. However, during separation some fine sediment particles are lost, thus decreasing the amount of sediment for the subsequent steps and lowering the measured phosphorus concentrations. It was decided for data analysis that

the sum of the phosphorus fractions would be classified as the TP in the sediment.

Extracts from the steps in the sequential process were tested for orthophosphate on the QuikChem FIA+ 8000 series Lachat auto analyzer, which uses the ascorbic acid colorimetric method. Samples from the NaOH and HCl extraction steps were neutralized with 2.0 N HCl and 1.0 M NaOH, respectively, before analysis. Concentrations of orthophosphate are translated to a mass of phosphorus per mass of sediment, and adjusted to the dry weight of the sediment by multiplying the wet weight phosphorus mass by the percent solids (1- Moisture Content).

3.5 Data Analysis

3.5.1 Phosphorus Flux Calculations

The sediment-water flux, or release rate, of orthophosphate in the mesocosms was calculated from the equation:

$$Flux = \frac{dC}{dt} = D\frac{d^2C}{dz^2} \tag{3.1}$$

where C is the average concentration in the water column, t is time, L is the total depth of the water in the mesocosm, and D is the diffusion coefficient for phosphate in water.

For mesocosms where a phosphorus gradient was evident due to limited mixing, a mass balance around the sediment and water column (Equation 3.2) was used to

calculate the average concentration in the water column where it was assumed that the orthophosphate concentration gradient was diffusive from the sediment, and constant with time. The solution was optimized by iteratively minimizing the sum of squares between measured and calculated orthophosphate concentration for each sampling event at the two different measurements along the water column. For each data set, coefficients A and C_0 were calculated from the iterative process.

$$C = A[\frac{1}{2}z^2 - Lz] + C_0 \tag{3.2}$$

where C is the orthophosphate concentration at z height above the sediment, A is a function of the diffusion coefficient (D) of orthophosphate, and C_0 is the concentration of orthophosphate at the sediment water interface.

Once coefficients A and C_0 were calculated for each sampling event, the average concentration in the water column was calculated by integrating Equation 3.2 and dividing over the length of the water column to obtain Equation 3.3. When the water columns were completely mixed, C_{ave} is the concentration of the water samples taken.

$$C_{ave} = \int_0^L C dz \cdot \frac{1}{L} = C_0 - \frac{A}{3}L^2 \tag{3.3}$$

The overall flux for the water column (column mass flux) was obtained by plotting the C_{ave} versus time. A linear regression was fit through the data, and the slope times

L is equal to the mass flux rate. During phase 1 (with pond water), the data tended to deviate from the straight line at roughly 14 days, due to bacterial growth in the columns, as indicated by a difference between TP and orthophosphate measurements. This was not observed in phases 2 and 3, when the mesocosms were flushed with synthetic runoff and the data did not deviate significantly from the initial linear fit. The mass flux rate was therefore calculated for the first 14 days in phase 1 and 30 days in phases 2 and 3.

3.5.2 Dissolved Oxygen Model

As discussed in the review section, DO concentration is an important parameter for orthophosphate release from the sediments. The Michaelis-Menten kinetic model, which assumes that bacterial oxygen demand is dominant over chemical oxygen demand (Michaelis and Menten 1913, translated by Johnson and Goody 2011), was fit to the DO as a measure of sediment oxygen demand (SOD):

$$S = \frac{S_{max}[C_{O2}]}{K_M + [C_{O2}]} \tag{3.4}$$

Where S is the substrate consumption rate, S_{max} is the maximum dissolved oxygen consumption rate, C_{O2} is the substrate (oxygen) concentration, and K_M is the half-consumption concentration. A constant K_M of 1.4 mg/L was used for all of the mesocosms when fitting the model, as reported by Walker and Snodgrass (1986) from a regression of 60 sediment types. The coefficient S_{max} was then found from a fit of the DO data.

Chapter 4

Results

4.1 Pond Field Data

When sampling was conducted, it was clear that the ponds were biologically active. Ponds B, C, and D had heavy duckweed growth on the surface that prevented light from penetrating through the water column. Pond A did not have duckweed growth, but the water column had suspended green particulate matter. From the DO profiles taken at each sampling location given in Figure 4.1, the DO dropped below 1 mg/L at 0.5 m below the water surface in ponds B, C, and D and was less than 0.5 mg/L at the bottom. These ponds are well sheltered by trees and other heavy vegetation, which prevents wind mixing of the pond. Pond A had high DO up to 0.8 m below the water surface, but dropped to below 0.5 mg/L after 0.8 m. The exact bottom of the sediments was hard to determine because of an unconsolidated layer at the sediment

surface. In pond A, only the bottom measurement had low DO, suggesting that the measurement may be in the sediment. Ponds B, C and D show more than one depth with low DO, indicating stratification in the ponds. During summer sampling events, TP concentration was 0.056 mg/L in pond A, 0.24 mg/L in pond B, 0.135 mg/L in pond C, and 0.525 mg/L in pond D. The TP levels in the ponds follow the predicted responses to stratification in the ponds. Pond A has low TP, and high DO because it was mixed.

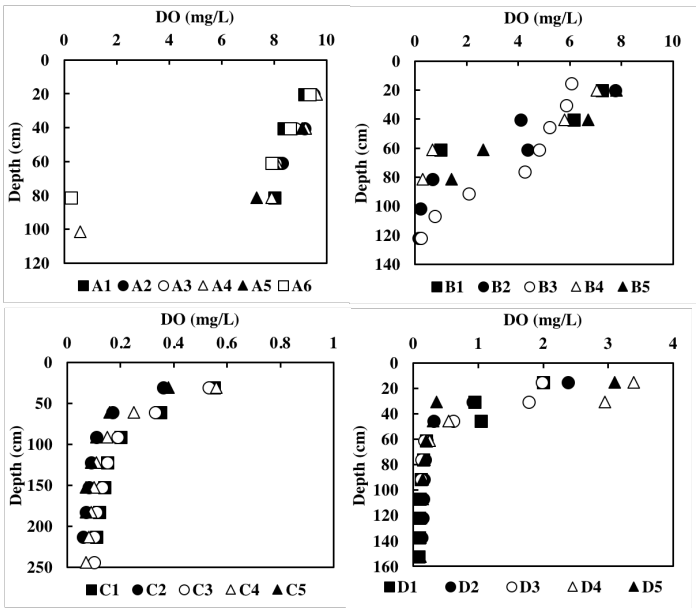

Figure 4.1: Dissolved oxygen concentration profiles at the different sampling locations in each pond.

From the field measurements, it is clear that the individual ponds experience different DO trends. Pond A had high DO throughout the water column, until depths past 80 cm, which may have been in the mucky surface of the sediments. High DO indicated

that the water column was well mixed, but the mesocosms from pond A experienced rapid DO decrease. Wind-mixing of the pond may explain the high DO in the field, while the unmixed mesocosms showed the opposite. Pond B field measurements showed stratification in the pond, suggesting that the pond is not well mixed. This may be indicative of high phosphorus release, as the bottom layer of the pond may remain anoxic for long periods of time unless flushed. The mesocosm DO results from pond B show high DO consumption rates, which would result in anoxia in the unmixed layer of the water column. Ponds C and D showed very low DO in the field throughout the water column, but did not experience a rapid decrease in the mesocosms as ponds A and B did. The aerobic condition of the first phase was unintentional, as the mesocosms were expected to consume all oxygen and become anaerobic.

4.2 Dissolved Oxygen Concentration in Mesocosms

During phase 1, the water column was relatively undisturbed in the mesocosm. This was done to examine if the sediments could cause anoxia when the ponds were unmixed, simulating periods between rain events with low or no flow in the ponds. There was limited mixing present as the DO probe was placed into the mesocosm once per day from the top of the column and bubbles of gas were released from the sediments, rising through the water column. Figure 4.2 shows the DO data at 8 cm above the sediment surface, and how it changes over time in phase 1 for each pond.

In pond A, the DO concentration drops rapidly, reaching below 1 mg/L after 2 days.

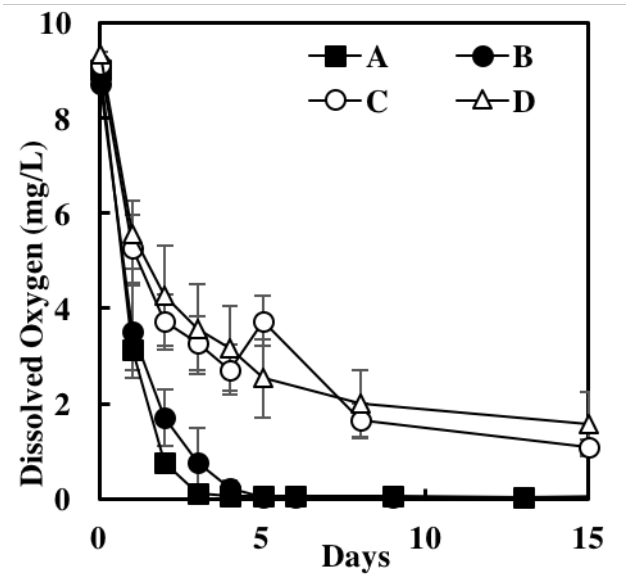

Figure 4.2: Average dissolved oxygen concentration for each pond over the Phase 1 sampling period with an unmixed water column. Measurements were taken at 8cm above the sediment (Error bars=1SD).

The DO in pond A remains very low (<0.1 mg/L) throughout the rest of phase 1. Pond B exhibits a similar trend, reaching 1 mg/L after 3 days, and less than 0.1 mg/L for the rest of phase 1. DO in ponds C and D do not decrease as rapidly as ponds A and B, and only reach an average of 1.09 mg/L (± 0.32 SD) and 1.58 mg/L (± 1.37 SD) at the end of the phase. It is interesting that field measurements for ponds C and D indicated the lowest DO concentration at the pond bottom.

Along with DO, pH was monitored in the mesocosms. The pH ranged from 6.58 to 8.35 in the first phase, where it started high and decreased throughout the monitoring. In phases 2 and 3, the pH remained relatively constant, ranging from 7.3 to 9.5. This range is lower than the reported thresholds by Koski-Vähälä et al. (2001) and Wu et al.

(2014), where pH affects phosphorus release. pH time-series data is given in Appendix B.

A quantification of sediment oxygen demand can be achieved from the Michaelis-Menten model. The coefficient S_{max} is the maximum oxygen consumption by the biologically active sediments. The model was fit to data from individual mesocosms. Assuming a constant K_M of 1.4 mg/L, S_{max} was calculated for each mesocosm, as given in Table 4.1, along with the average and 67% confidence interval of the mean for each pond.

The mean S_{max} for each pond follows the trends observed in Figure 4.2 with the dissolved oxygen data. Ponds A and B showed fast oxygen consumption rates. Ponds C and D had similar oxygen consumption rates of 1.94 ($\pm$ 0.19) g/m^2/day and 1.85 ($\pm$ 0.63) g/m^2/day, respectively. The variability between mesocosms is evident within ponds C and D, where the ranges of S_{max} are from 1.42 to 2.43 g/m^2/day and 0.94 to 4.10 g/m^2/day, respectively. The low DO in mesocosms from ponds A and B indicates that the potential for phosphorus release is greater than that of ponds C and D (Patrick and Khalid, 1974; Wu et al., 2014).

Table 4.1: Michaelis-Menten maximum oxygen consumption rate (S_{max}) for mesocosms. CI is confidence interval of the average oxygen consumption rate.

Mesocosm	S_{max} ($g/m^2/day$)
A1	5.79
A2	3.13
A3	4.14
A4	4.87
A5	4.40
A6	2.94
Average ± 67% CI	4.21 ± 0.53
B1	3.56
B2	2.13
B3	7.34
B4	4.28
B5	3.84
Average ± 67% CI	4.23 ± 0.95
C1	2.43
C2	2.11
C3	2.05
C4	1.72
C5	1.42
Average ± 67% CI	1.94 ± 0.19
D1	4.10
D2	1.38
D3	1.36
D4	0.94
D5	1.47
Average ± 67% CI	1.85 ± 0.63

A relationship between oxygen consumption and phosphorus release from the Phase 1 mesocosms is presented in Figure 4.3 to determine whether oxygen consumption rate (S_{max}) in the ponds can be used to predict and quantify phosphorus release from the sediments. The rationale is that both S_{max} and phosphorus release (RR) would be influenced by the organic content of the sediments, so the relationship would be of a related process. The data is plotted in Figure 4.3. The linear regression of the data is given in Equation 4.1, with an intercept of zero. The plot suggests that a relationship does exist between the maximum oxygen consumption rate in the sediments and phosphorus release.

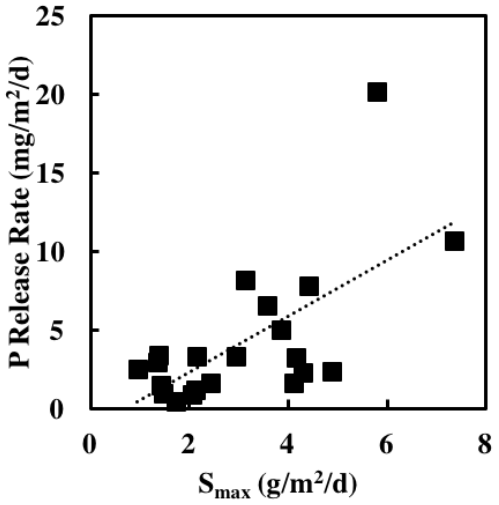

Figure 4.3: Phase 1 phosphorus flux versus maximum oxygen consumption rate in the sediments

$$RR = 1.46 S_{max} \ (R^2 = 0.41) \tag{4.1}$$

4.3 Phosphorus Release

Before the start of phase 1, the concentrations of orthophosphate decreased to low levels because of the air bubbling in the water column. During phase 1, orthophosphate concentrations increased in all mesocosms. An example of the phosphorus data collected over the 30 day monitoring period in phase 1 is shown in Figure B.2 for pond A. The full set of plots for each monitoring period are given in Appendix B for each pond and phase.

The orthophosphate concentration increase in the water columns of ponds A and B were approximately linear followed by a decrease in concentration. The decrease is believed to have been caused by a growth of microbial population in phase 1 of the mesocosms that removed orthophosphate. This hypothesis is substantiated by total phosphorus measurements which were, on average, 90.8 μg/L higher than orthophosphate, which is the same magnitude of the orthophosphate deviation from linearity for most mesocosms. Some mesocosms developed a visible growth on the walls of the polycarbonate tube after approximately 40 days, which also accounted for a decrease in orthophosphate and greater disparity between TP and orthophosphate concentrations. The decrease in slope of concentration-time curves did not appear until after 14 days, so this period was used to compute the orthophosphate release, as given in Table 4.2 using Equations 3.2 and 3.3. Release rates for phase 2 and phase 3 were calculated based on the entire sampling period length (23 to 35 days) because the orthophosphate concentration increase followed a linear trend. The release rates for each mesocosm and

phase are listed in Table 4.2.

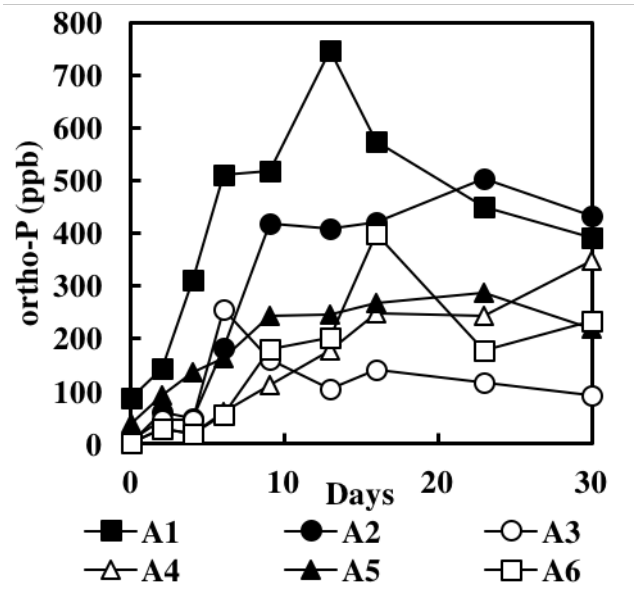

Figure 4.4: Phosphorus concentration (orthophosphate) above sediment-water interface of pond A mesocosms during phase 1. Mesocosm A5 was visibly different from the rest, as it was mostly sand and near the second inlet.

Phase 1 showed significant orthophosphate concentration increase over the course of the monitoring period. The maximum orthophosphate concentrations in pond A mesocosms in the 30 day period range from 254.8 to 747.3 μg/L. Mesocosm A5, which was mostly sand, did not seem to be an outlier in orthophosphate concentrations, although the rate computed from Figure B.2 was towards the lower end of pond A. For pond B, the maximum concentrations at the bottom of the water column range from 147.1 to 381.5 μg/L. Ponds A and B also experienced periodical spikes in water column concentration, but after these spikes the concentration would typically return to its previous trend. Overall, the orthophosphate concentration change in the water columns of

pond A and pond B mesocosms were highly variable, with release rates ranging from 2.29 to 20.14 mg/m^2/day. Ponds C and D showed significantly less orthophosphate concentration increase in the water column throughout the 30 day monitoring period. Pond C showed some spikes in concentration, but the overall trend was linear. The final 30 day concentrations at the bottom of the water column ranged from 22.7 to 68.2 μg/L in pond C, resulting in a low average release rate of 1.12 ($\pm$ 0.20) mg/m^2/day. Concentrations at the end of 30 days in the pond D mesocosms ranged from 10.8 to 246.3 μg/L measured at the bottom of the water column. Mesocosm D5 showed almost no orthophosphate increase, while mesocosm D1 showed an increase with similar magnitude to ponds A and B. The rest of the mesocosms from pond D had final concentrations less than approximately 100 μg/L, with a low average release rate of 2.27 ($\pm$ 0.44) mg/m^2/day. Pond A showed the highest average phosphorus release rate in phase 1, followed by B, D, and C. The range of release rates, however, for ponds A and B are much larger than ponds C and D, suggesting that more than the dissolved oxygen concentrations influence sediment phosphorus release.

Phase 2 orthophosphate increase was less in ponds A and B and greater in ponds C and D than in phase 1. The rate of increase was linear for the 35 day monitoring period, but was sometimes negative for certain mesocosms from ponds A and B. The starting orthophosphate concentration in the water column from the synthetic stormwater in A and B was 138 μg/L, and the final concentrations ranged from 27.4 to 425.3 μg/L in pond A and 85 to 188.8 μg/L in pond B. The average release rates for ponds A and

B were 3.10 (± 2.34) mg/m^2/day and -0.44 (± 1.28) mg/m^2/day, respectively. Ponds C and D started at the final concentrations of phase 1 because there was little release in phase 1. These starting concentrations range from 20.2 to 83.5 μg/L. Most of the mesocosms released orthophosphate in the water column linearly, but some released almost no phosphorus. The final concentrations range from 74.4 to 153.8 μg/L (2.86 ± 0.57 mg/m^2/day) in pond C and 32.6 to 201.9 μg/L (2.70 ± 1.24 mg/m^2/day) in pond D. It is possible that the negative release of orthophosphate is caused by the fact that the mesocosms were not flushed with organic material which would settle, be broken down by bacteria and supply a source of orthophosphate to the water column. If the available sediment orthophosphate was depleted, the water column could act as a source of orthophosphate to the sediment.

In phase 3, orthophosphate release was lower than in both phase 1 and 2. The initial orthophosphate concentration was 57 μg/L for all mesocosms from the synthetic stormwater flush. In pond A, half of the mesocosms showed negative phosphorus release over 35 days (A3, A4, A5), while in pond B two mesocosms showed negative release (B1, B2) and one showed an initial decrease in phosphorus, but then began releasing at 14 days (B5). Final mesocosm concentrations in the water column for pond A range from 5.1 to 239.4 μg/L and in pond B range from 7.2 to 81.2 μg/L. In pond C, two columns showed a net-zero phosphorus release over 23 days (sampling period length) and in pond D three columns showed negative phosphorus release. The final mesocosm concentrations in ponds C and D range from 53.8 to 132.8 μg/L and 11.5 to 156.7 μg/L,

respectively. The phase 3 release rates for each pond are significantly lower than in phases 1 and 2 for ponds A, B, and D, but slightly higher in some pond C mesocosms. This suggests that the flushing between each phase negatively impacted the sediment ability to release phosphorus.

Table 4.2: Mesocosm phosphorus release rates in mg/m^2/day (CI is the confidence interval of the average).

Mesocosm	Phase 1	Phase 2	Phase 3
A1	20.14	9.24	5.29
A2	8.15	1.76	4.76
A3	3.26	-0.97	-1.59
A4	2.35	-2.96	-1.40
A5	7.77	4.15	-0.40
A6	3.31	7.35	2.78
Average±67% CI	7.50±2.94	3.10±2.34	1.57±1.54
B1	6.58	2.81	-1.76
B2	3.28	-0.64	-1.71
B3	10.65	0.50	1.14
B4	2.29	-2.29	0.96
B5	5.04	-2.58	0.26
Average±67% CI	5.57±1.45	-0.44±1.28	-0.22±0.82
C1	1.61	2.51	1.67
C2	1.21	4.21	0.05
C3	0.91	3.54	4.27
C4	0.44	2.10	0.74
C5	1.45	1.93	0.08
Average±67% CI	1.12±0.20	2.86±0.57	1.36±1.02
D1	1.60	4.24	-2.54
D2	3.38	3.45	5.52
D3	2.94	2.31	-2.10
D4	2.50	-0.83	-1.84
D5	0.93	4.34	2.28
Average±67% CI	2.27±0.44	2.70±1.24	0.26±2.04

4.4 Sediment Phosphorus Concentration

Before sediment phosphorus was quantified, sediment characteristics including water content and organic matter content were determined on a subsample of the extruded intervals. Water content was used to convert wet weight to dry weight phosphorus concentrations during the sequential extraction, and organic matter content gives an indication of particulate loading in the ponds. The water contents ranged from 15 to 92% by weight for pond A, 88 to 99% by weight for pond B, 23 to 98% by weight for pond C, and 38 to 90% by weight for pond D. The water content tended to decrease with depth in the sediment. The organic matter contents ranged from 3 to 57% by dry weight for pond A, 72 to 92% by dry weight for pond B, 3 to 40% by dry weight for pond C, and 6 to 34% by dry weight for pond D. Pond B had the highest organic matter content, and pond D had the lowest. Mesocosm A5 was much sandier in composition, and had lower organic matter and water content than the rest of the mesocosms from pond A. The complete set of data is given in Appendix C. No strong correlation between organic matter content and sediment phosphorus release rate was observed.

Sediment phosphorus analysis was conducted by extracting six different forms of phosphorus bound to different compounds in the sediment, as defined in Section 3. The forms of phosphorus most relevant to pond sediments and phosphorus release are loose-P and Fe-P. These two forms are considered mobile, meaning these forms are what compose phosphorus released into the water column. Loose-P is the phosphorus found in the porewater of the sediments and that associated with $CaCO_3$, and can move freely

in the sediments and water column. Fe-P indicates the potential for release under anoxic conditions when iron is reduced. Other forms of phosphorus are not as readily available for release into the water column. These forms include Al-P, mineral-P, labile-P, and residual-P. Al-P is phosphorus adsorbed to amorphous aluminum hydroxides ($Al(OH)_3$), which dissolves under high NaOH concentrations that correspond with high pH (>9). Mineral-P is calcite and apatite bound phosphorus, only released by acid dissolution. Labile-P is the organic mobile fraction in the sediments, but not biologically available, and residual-P is the recalcitrant phosphorus remaining at the end of the sequential extraction process, assumed to be organic. The analysis was conducted from 0 to 11 cm at 1 cm intervals up to 5 cm, and then in 3 cm up to 11 cm. The concentrations measured for each interval are given at the midpoint of the interval (i.e. for 0-1 cm, concentration given at 0.5 cm).

Averages for each depth interval and each species of phosphorus in the sediment for pond A are given in Figure 4.5. Individual mesocosm sediment phosphorus data is given in Appendix C. The organic associated species (labile and residual combined) are the largest fraction at 56% of the total phosphorus (averaged between 0 and 4 cm). Next largest (0 to 4 cm) is the mineral-bound phosphorus fraction (18%), followed by aluminum-bound (14%), iron-bound (12%), and loosely-bound and CaCO3 bound P (labelled as loosely bound P). For mesocosms from pond A, the loosely bound phosphorus is below the limit of detection for phosphorus (10 μg/L). All of the other phosphorus fraction concentrations are highest per kg of sediment at the surface intervals of the

sediment. The concentrations generally decrease with depth in the sediment. The individual mesocosms in pond A showed similar trends, except A5, the core with a sandier appearance, which had low residual organic phosphorus and a high mineral bound phosphorus. The variability in total phosphorus was high between the mesocosms, indicating that phosphorus speciation was spatially variable. Additionally, with large fractions of organic phosphorus there is a significant pool of phosphorus to be broken down and released.

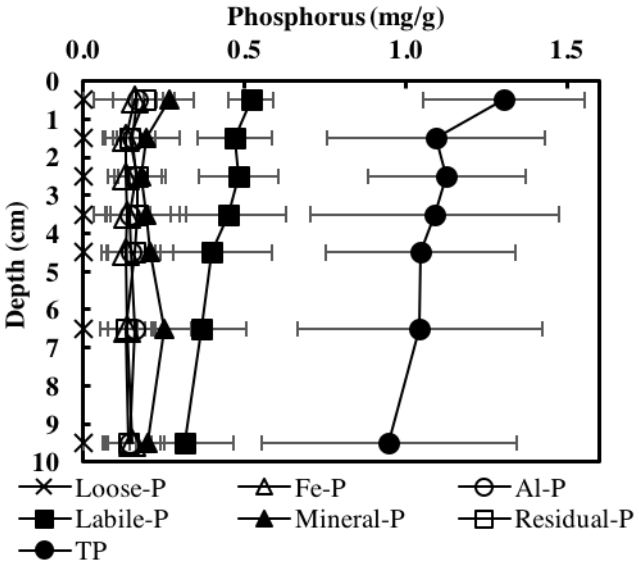

Figure 4.5: Phosphorus fractions from sequential extraction analysis for mesocosms in pond A (Error bars=±1SD)

The average phosphorus fractions with depth from pond B are given in Figure 4.6. Pond B had substantially higher organic phosphorus fractions than the other mesocosms (64%), specifically mesocosm B5 had over 1 mg/g labile-P in the 0-1 cm interval. B5 also showed a spike in all fractions of phosphorus concentration at interval 3-4 cm in

both labile-P and Fe-P, which is evident in Figure 4.6. Fe-P (17%) was the second highest after labile-P in the near-surface centimeter of the sediments in the mesocosms from pond B, followed by mineral-P (7%), Al-P (6%), and loose-P (5%). Pond B had measurable loose-P, unlike pond A. The variability in pond B is larger than in pond A at some depths, as is evident by the standard deviations. The organic fraction of phosphorus, specifically labile-P, was the most variable between mesocosms. The phosphorus concentrations are relatively constant between 4 and 11 cm, indicating that the total pool and speciation does not change rapidly. Additionally, there is evidence that indicates a large input of phosphorus in the past as indicated by the spike of phosphorus between 3 and 4 cm. This phosphorus pool can move upward through the sediment as mobile phosphorus and released into the water column. The spike of phosphorus, however, would move downward as particles are deposited on the surface.

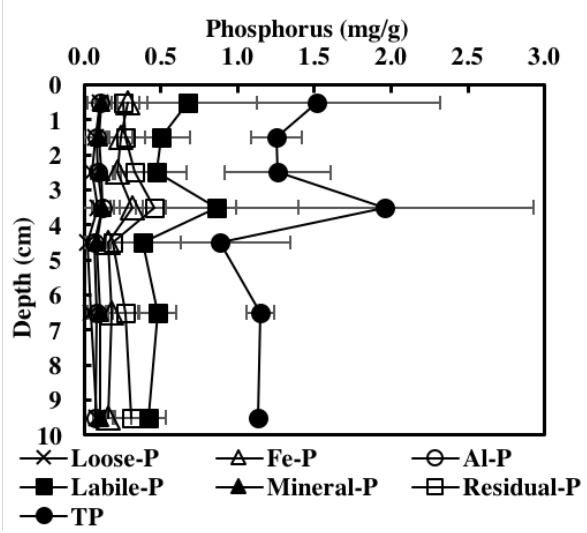

Figure 4.6: Phosphorus fractions from sequential extraction analysis for mesocosms in pond B (Error bars=±1SD)

The average phosphorus fractions from pond C are given in Figure 4.7. The magnitudes of the phosphorus fractions are less than ponds A and B (approximately half of pond B). Above 4 cm in the sediment, the significant fraction is labile-P (35%). Residual-P (18%), Fe-P (14%), Al-P (14%), and mineral-P (19%) are approximately the same magnitude. Below 4 cm, the fractions remain relatively constant except labile-P, which decreases as the dominant fractions become mineral-P and Al-P. Most likely, the organic phosphorus in the older, deeper sediment layers has been converted to other forms over time. The deeper phosphorus fractions, once mobile, may also move upward through diffusion toward the water column along a concentration gradient. There was no measurable loosely bound phosphorus in pond C. The variability between mesocosms in pond C is much lower than in ponds A and B, indicating that the sediment is spatially similar in the pond.

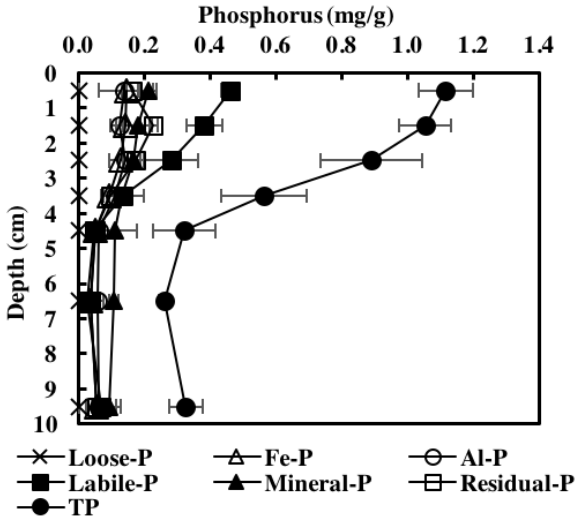

Figure 4.7: Phosphorus fractions from sequential extraction analysis for mesocosms in pond C (Error bars=±1SD)

The average phosphorus fractions from pond D are given in Figure 4.8. Like the rest of the ponds, the largest phosphorus fraction in the near-surface of the pond D mesocosms is the total organic phosphorus (sum of labile-P and residual-P, 55%). The top few centimeters have the highest phosphorus concentrations, but below three centimeters the fractions remain relatively constant. Some loose-P was measured in the 8-11 cm interval, suggesting stores of phosphorus deeper in the sediment layers, but not available at the sediment-water interface. The Al-P and mineral-P have similar concentrations in the top four centimeters (17%), and Fe-P is the lowest fraction (11%) of the three. The variability in phosphorus fractions between mesocosms is high in pond D, mainly in the organic fractions. If organic phosphorus is broken down into bioavailable forms, mesocosms with high organic phosphorus may release more phosphorus. After 3 cm, the phosphorus fractions stay relatively constant, indicating that changes in speciation may not change rapidly and may have reached an equilibrium because there is little gradient with depth.

The phosphorus concentrations were averaged for 0 to 4 cm to simplify comparison between mesocosms (Figure 4.9) and to reported literature data. Additionally, the top centimeters are the most directly interactive with the water column. Labile-P is the largest fraction in each pond. Only pond B had measurable loose-P, and had the highest Fe-P and organic fractions. Both ponds C and D had less TP than ponds A and B.

Fe-P and loose-P are the two redox sensitive fractions of phosphorus that can interact with phosphorus in the water column. Labile-P may become available after some

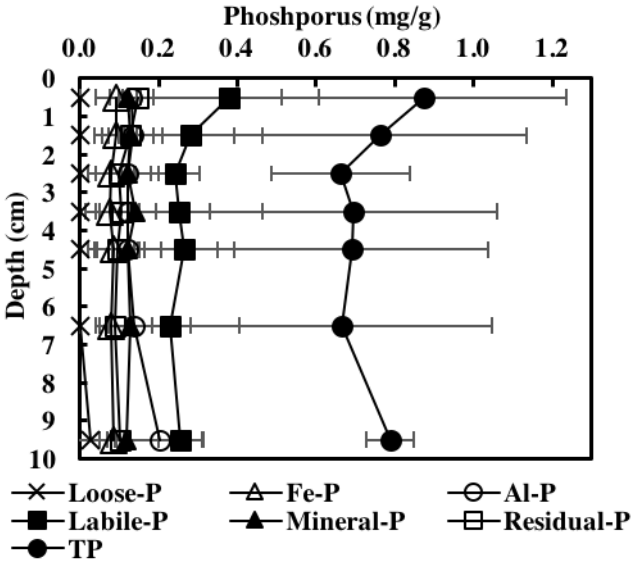

Figure 4.8: Phosphorus fractions from sequential extraction analysis for mesocosms in pond D (Error bars=±1SD)

time, but must be broken down first by microbes to a more bioavailable form (typically orthophosphate) and may be adsorbed by one of the minerals in the sediment. The average Fe-P concentrations were 0.14, 0.26, 0.13, and 0.08 mg/g (dry weight) for ponds A, B, C, and D, respectively. The labile organic phosphorus concentrations were 0.48, 0.63, 0.31, and 0.29 mg/g (dry weight) for ponds A, B, C, and D, respectively.

The phosphorus fractions in the sediment can reveal information about the potential phosphorus release trends that may be seen. Because Fe-P is considered redox sensitive, and thus can become mobile, a large fraction in the sediments suggests that phosphorus release is highly dependent on redox conditions in the water column and sediment (i.e., dissolved oxygen concentrations). If one considers that the density of sediment and water is roughly 2 kg/L, and the ratio of dry to wet sediment is 0.23 on average,

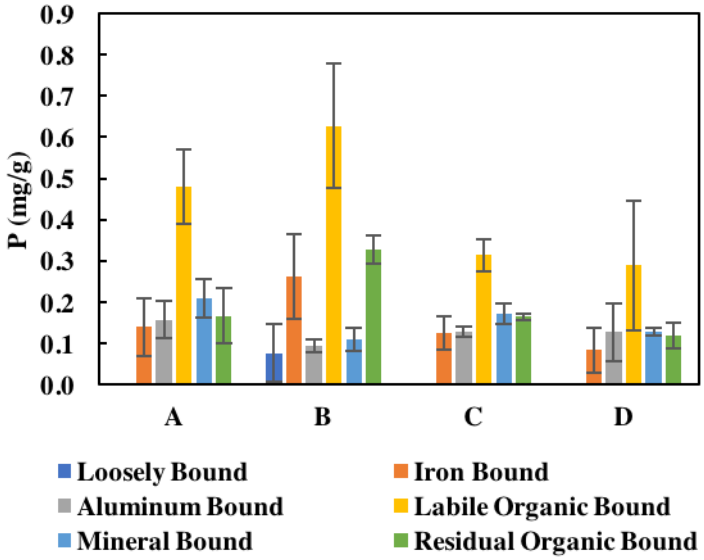

Figure 4.9: Average phosphorus fraction concentrations from 0 to 4 cm

the equivalent concentration in the water column of 200 mg/kg would be roughly 23 mg/L. It is apparent from the scales of water-phase and sediment-phase phosphorus concentration in Figures 4.9 that the redox-sensitive phosphorus in the sediments can supply substantial phosphorus to the water column.

4.5 Phosphorus release rate versus sediment phosphorus

The phosphorus release rates (RR) calculated for the pond mesocosms (based on orthophosphate, which is equal to TP) plotted in Figure 4.10 against the measured redox sensitive phosphorus (loose-P and Fe-P) averaged from 0 to 4 cm resulted in a relationship defined by Equation 4.2. The correlation for the regression suggests that there is a clear relationship between redox-P and orthophosphate release. Mesocosm B5 was

excluded from the regression fit because it had a large influence on the fit of the line and was a significant outlier ($p<0.05$).

$$RR = 32.099(redox\ P) + 0.8637\ (R^2 = 0.2) \tag{4.2}$$

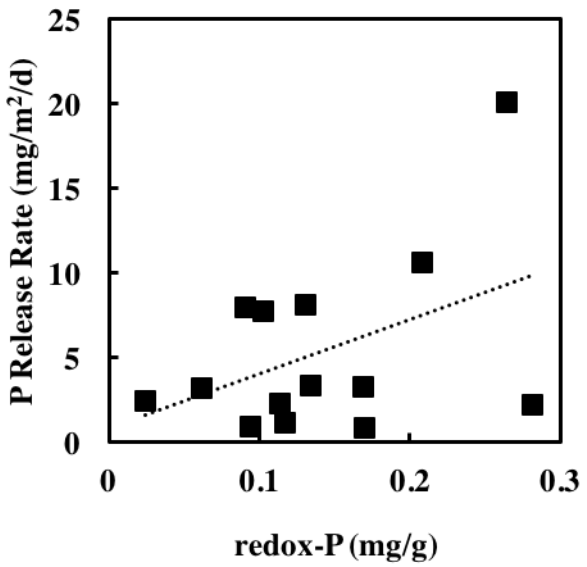

Figure 4.10: Phase 1 phosphorus release versus the 0 - 4 cm average of sediment redox-P (loose-P and Fe-P) in mg/g. Mesocosm B5 was excluded from the regression fit because it had a large influence on the fit of the line and was a significant outlier ($p<0.05$).

Given the large stores of organic compound in the sediments of these ponds, especially in older ponds like the ones included in this study, the labile-P from the pond sediments was added to loose-P and Fe-P and plotted against the phosphorus release rates in Figure 4.11. A linear regression was fit to this data (Equation 4.3). This sum of labile-P, loose-P, and Fe-P is defined hereafter as mobile-P. Mesocosm B5 was excluded

from the regression fit because it had a large influence on the fit of the line and was a significant outlier ($p<0.05$).

$$RR = 12.61(mobile\ P) - 1.6261\ (R^2 = 0.2) \tag{4.3}$$

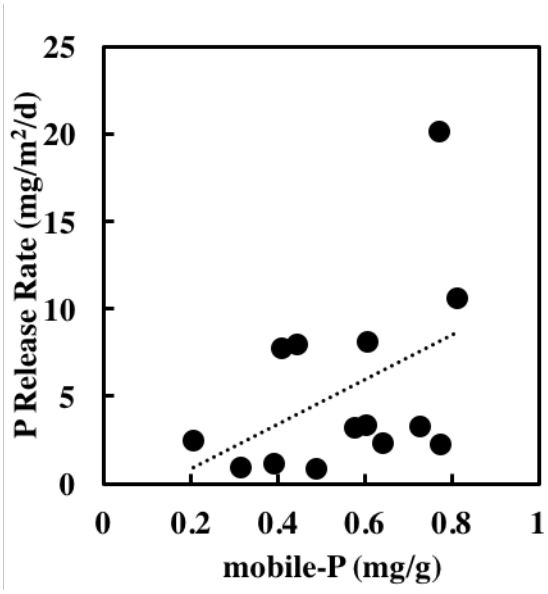

Figure 4.11: Phase 1 phosphorus release versus the 0 - 4 cm average of sediment mobile-P (loose-P, Fe-P, and labile-P) in mg/g. Mesocosm B5 was excluded from the regression fit because it had a large influence on the fit of the line and was a significant outlier ($p<0.05$).

Chapter 5

Discussion

From the results, phosphorus release in ponds can be linked to three characteristics of ponds: organic phosphorus and bacterial activity, spatial location within a pond, and the flushing of the water column above pond sediments. These relationships can lead to predictive measures in understanding when phosphorus release will occur, at what magnitude it will occur, and if it will continue.

5.1 Phosphorus release dependence on organic phosphorus and bacterial activity

Several observations from the experiments conducted on the mesocosms suggest that organic phosphorus, specifically labile organic phosphorus, can increase phosphorus release from the sediments through high biological activity in the sediments. The first

indication of this relationship is the rate of drop in DO concentration. DO consumption is indicative of aerobic microbial activity, predominantly in the substrate-rich sediments (Holdren and Armstrong, 1980; Cooke et al., 1993; Engstrom, 2005). The oxygen consumption rates calculated with the Michaelis-Menten model were high, and showed a positive relationship with P release (Figure 4.3).

One factor that drives biological oxygen consumption is the degradation of organic matter, which would include degradation of organic phosphorus. Organic phosphorus has been identified as a potentially important fraction of phosphorus in internal loading, and can originate from bacterial communities and degradation of organic matter as polyphosphate and transformed to orthophosphate during mineralization (Gächter et al., 1988; Hupfer et al., 2004; Hupfer and Lewandowski, 2008; Ahlgren et al., 2011; Song et al., 2017). Organic phosphorus can have a large impact in older ponds, as Reitzel et al. (2007) have cited half-lives ranging from 0.8 to 13 years depending on whether the phosphorus is soluble colloidal or particulate, and its compound group. A 1-year half-life, for example, means that 8% of the compound would degrade in 30 days. This concept is in contrast to previous hypotheses that assume phosphorus release is primarily redox driven.

However, even under the same redox conditions, the pond phosphorus release rates were different from the lake release rates. The slope of the overall regression between redox-P and P release is approximately two times larger in ponds (Equation 4.2) than

Pilgrim and Nürnberg's models (Equations 2.2 and 2.3), suggesting that there is another source of phosphorus besides redox sensitive phosphorus. Comparing the labile-P fractions of phosphorus in ponds to lakes, the ponds in this study had almost double the labile-P concentration than reported in lake studies by Williams et al. (1976), Gonsiorczyk et al. (1997), Bai et al. (2009), and James (2011). With a higher fraction of organic phosphorus available for mineralization by a strong microbial presence, the potentially releasable phosphorus fraction in the sediments is larger. Organic phosphorus loading to ponds may increase the amount of available phosphorus to be released. In watersheds with higher development, more runoff may introduce greater amounts of organic matter to the ponds. Additionally, ponds may become overloaded with material. The regression shown as Equation 4.3 between mobile-P (loose-P, Fe-P, and labile-P) and phosphorus release rates compares well against the lake release rate models and shows a positive relationship between mobile-P and P release, suggesting that organic phosphorus can have an impact on phosphorus release.

5.2 Spatial variability of phosphorus release

It was originally hypothesized that phosphorus release is spatially variable, depending on the location within the pond and the structural features of the pond (inlet, outlet). James (2011) cites horizontally spatial variations in sediment phosphorus fractions and phosphorus release within a shallow oxbow lake, suggesting the potential for ponds to

experience a similar phenomenon. It was confirmed from this analysis that pond phosphorus release rates are also spatially variable. The phosphorus release from phase 1 of the experiments was plotted inside a spatial representation of the ponds to determine if a visual correlation could be made between sampling location and phosphorus release. The release rates are represented in Appendix B as Figures B.18 to B.21. The release rates are represented as points sized relative to each other for the comparison of magnitude.

Phosphorus release rates from pond A show that the highest release occurs near the west inlet and the outlet, away from the east area of the pond. The sediment in the west end was visibly muckier, while the sediment in the east end was visibly sandier, suggesting that the inlet on the west end deposits more organic material. This inlet receives runoff from a large park and parking lot. The release rates from pond B show that the middle sampling location had the highest phosphorus release, while the west portion of the pond had much lower release. However, there is only a slight difference between release rates at the inlet and the outlet. There is some indication of a path of high organic material deposition between the inlet and outlet. The phosphorus release rates in pond C from phase 1 were all relatively low compared to the other ponds, not exceeding 2.55 $mg/m^2/day$. The highest phosphorus release occurred near the inlet, but was not much larger than the release at the outlet. Aside from the inlet having high release rates, these results indicate no correlation of location and sediment phosphorus release rates in pond C. Finally, in pond D the phosphorus release rates were all similar

in magnitude, except the fifth sampling location just north of the outlet.

From the plots, there is no strong evidence that location within a pond correlates with phosphorus release from sediments. This is potentially due to the small size of the ponds, compared with lakes, in that organic particle settling does not change substantially across the flow path of the pond, but rather the size distribution of particles is approximately the same across the pond. To understand the pond holistically, measurements should be made in several locations, such that the uncertainty of the average release is sufficiently small. Furthermore, it is difficult to prioritize the location of pond maintenance activities to remediate sediment phosphorus release, such as specific inlet and outlet dredging or location of chemical treatment application, based on location within the pond.

5.3 Effect of synthetic flushing events on phosphorus release

The decrease in phosphorus release rates from most mesocosms between each phase in the experiment suggests that flushing of the water column has a substantial impact on future phosphorus release. These trends are evident in Table 4.2. Das et al. (2012) conducted flushing experiments on agricultural canals and found that phosphorus release rate decreased with flushing events. The initial phase, where no flush occurred before monitoring, had the highest average release compared to the other two phases in ponds

A and B. The negative release rates in pond B mesocosms imply that when the water column is flushed with high P concentration water, the added dissolved phosphorus mass in the influent stormwater may diffuse along a concentration gradient back into the sediments. If the mobile phosphorus is completely released during an anoxic period in the pond and a large storm removes most of the mass via flushing, then the overall release may decrease. However, the synthetic water that the mesocosms were flushed with did not have any particulates. These particulates in a real pond are a significant source of phosphorus to the pond; without them the only phosphorus sources are mobile phosphorus from the sediments and influent dissolved phosphorus. Organic phosphorus, as already discussed, can act as an orthophosphate source once degraded. Without particulate phosphorus accumulation, the breakdown of organic phosphorus already in the sediment into more bioavailable forms is the only source of phosphorus in the mesocosm. It is hypothesized that if particulate phosphorus is high in the influent water, phosphorus release may continue or even increase even if the pond is completely flushed by a large storm event. This means that, to be representative of the pond, a flushing event needs to contain organic particulates. Our flushing event did not.

In the mesocosms of ponds C and D, no flush occurred after the first phase, and the average release rate increased for both ponds. The likely reason is that the DO was decreased from aerobic (1-2 mg/L) to anaerobic (<0.3 mg/L) in the second phase by bubbling nitrogen gas. There was also no synthetic stormwater flush for ponds C and D between phases 1 and 2. Following the synthetic stormwater flush after phase 2 in

ponds C and D, both exhibited a decrease in average phosphorus release. The reasons for this decrease, as previously discussed, could include a lack of particulate matter in the synthetic stormwater and a negative phosphorus concentration gradient.

Chapter 6

Application

The findings of this thesis have important applications for ponds, especially those that are experiencing extreme eutrophication and releasing phosphorus and algae into receiving water bodies. Using information gathered from ponds in the field, the results can be used to determine if the pond is releasing large amounts of phosphorus or if it is performing as designed.

There are three main tools gleaned from this thesis to determine a pond?s efficiency and phosphorus release:

1. The DO consumption vs release relation,

2. The sediment phosphorus fractions vs release relations, and

3. Phosphorus flux and water column TP relationship

Perhaps the easiest (but least accurate) pathway to determine phosphorus release

in a pond would be to measure DO consumption after the water column is completely mixed, and during a period of minimal mixing. This can be done following the U.S.E.P.A. (2015) method. The maximum consumption (S_{max}) can be calculated from the Michaelis-Menten model (Equation 3.4). S_{max} is then input into the model Equation 6.1, which was plotted in Figure 4.3, to obtain an approximate phosphorus release rate.

$$RR = 1.46 S_{max} \tag{6.1}$$

where RR is the phosphorus release rate in mg/m^2/day and S_{max} is in g/m^2/day. The time for ponds to reach anoxia can also be calculated from S_{max} by using the initial DO concentration and an assumed 0.3 mg/L concentration of anoxic DO. Taking a mass balance around the water column:

$$h\frac{dC_{O_2}}{dt} = -S = -\frac{S_{max}[C_{O_2}]}{K_M + [C_{O_2}]} \tag{6.2}$$

the time to reach anoxia is given as:

$$t_{anoxic} = -\frac{K_M h}{S_{max}} ln \frac{[C_{O_2}]}{[C_{O_2}]_i} + \frac{h([C_{O_2}] - [C_{O_2}]_i)}{S_{max}} \tag{6.3}$$

where t_{anoxic} is the time a pond takes to reach anoxia in days, h is the water column height, $[C_{O_2}]_i$ is the initial dissolved oxygen concentration, $[C_{O_2}]$ is an assumed anoxic concentration of 0.3 mg/L, and the units on both sides of Equation 6.3 should match.

Another method to determine phosphorus release and pond performance would be to take a sediment sample with 4 cm depth and measure the loosely bound, iron bound, and labile organic phosphorus in the top four centimeters of sediment. These values can then be inputted into the models developed in this thesis (Equations 6.4 and 6.5) to find an approximate phosphorus release rate. The equation needed will depend on the sediment type and application of the result. For ponds with low organic matter, Equation 6.4 may be used because labile-P will not heavily impact the release rate. For ponds with high organic matter, Equation 6.5 may be used because labile-P can contribute highly to phosphorus release.

$$RR = 32.099(redox\ P) + 0.8637 \tag{6.4}$$

$$RR = 12.61(mobile\ P) - 1.6261 \tag{6.5}$$

where RR is the phosphorus release rate in mg/m^2/day, and mobile-P is the sum of loosely bound, iron bound, and labile organic phosphorus concentrations in mg/g.

The most accurate method of determining phosphorus release from stormwater pond sediments is to collect 5 to 6 mesocosms, using the methods described herein. Following

these methods, an average release rate with a confidence interval of the average can be determined and applied to the pond or ponds with similar characteristics. Additionally, the DO and sediment relationships provided above can be used as a secondary method for approximating phosphorus release.

Once phosphorus release is estimated, a mass balance on the studied pond can quantify the impact of phosphorus release on the pond total phosphorus concentration. A completely mixed batch reactor model that uses the phosphorus release rate to compute the total phosphorus in the pond after the number of days with no precipitation (antecedent period with no inflow), is given as Equation 6.6.

$$TP_t = TP_0 + \frac{RR}{z}(t - t_{anoxic}) \tag{6.6}$$

where RR is the phosphorus release rate in mg/m^2/day, z is the average pond depth in m, and TP$_t$ is the water column total phosphorus concentration in μg/L after the antecedent period, t, and TP$_0$ is the total phosphorus concentration at the beginning of the antecedent period

An example of the use of this model is given in Figure 6.1, where an average depth of 1.5 m was assumed along with a completely mixed water column where the TP concentration is spatially homogenous. If one measured a 100 μg/L difference in TP concentration after 5 anoxic days, the release rate would be 30 mg/m^2/day.

These application methods were designed to be simple and universal for users to

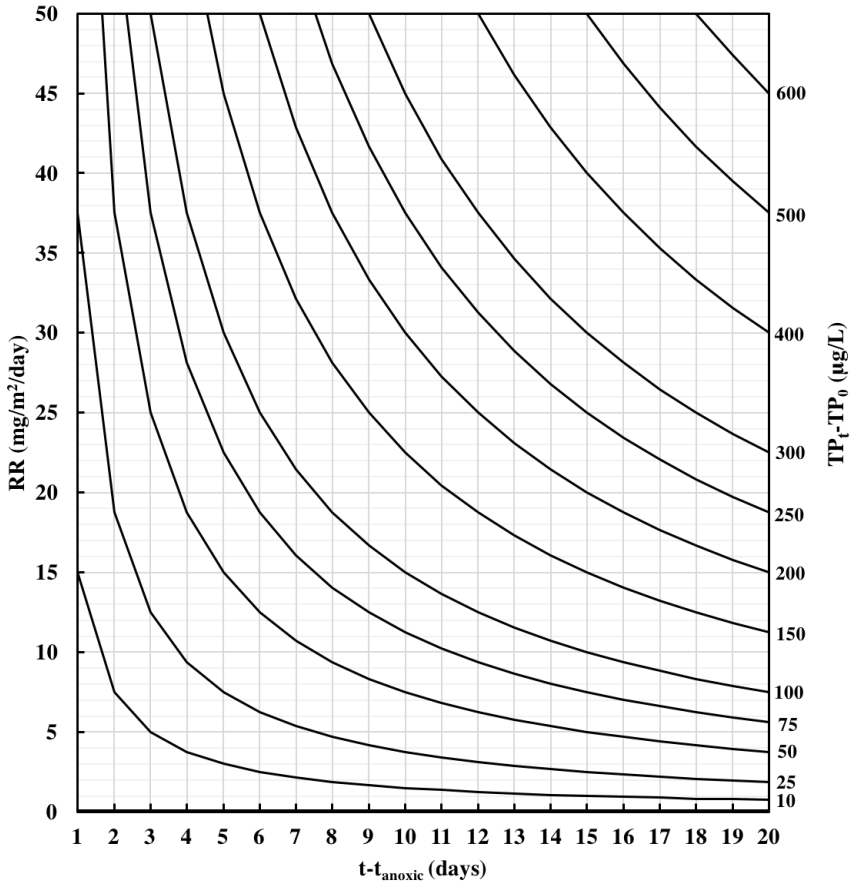

Figure 6.1: Phosphorus release rates (RR) for an example pond based on TP measurements and antecedent period in a pond.

easily assess ponds that may need maintenance. More complex monitoring may be needed if ponds do not meet the assumptions listed in this section such as if ponds are not completely mixed, if the storm event does not completely flush a pond, or if the pond has a complex inflow and outflow scheme. Ultimately, if ponds have phosphorus concentration in the water column which is above the inflow value, they are most likely releasing phosphorus from the sediments, and some form of maintenance action needs

to be taken into consideration.

Chapter 7

Conclusions

Studying the dynamics of phosphorus in stormwater retention ponds has revealed the impact that release of phosphorus from the sediments can have on the overall quality of water in the pond. From mesocosm studies and chemical analysis of water and sediment samples, it was found that:

1. Phosphorus release from pond sediments has a wide range of magnitudes
2. Dissolved oxygen in the water column heavily impacts phosphorus release, and is driven by biological activity in the sediments.
3. Sediment composition, specifically redox sensitive phosphorus and organic phosphorus in the sediment, have a positive relationship with phosphorus release.

Twentyone mesocosms were monitored for over three 30-day phases to understand phosphorus release dynamics from four different ponds. It was found that phosphorus

release was not uniform across all mesocosms, and thus is dependent on other characteristics of the mesocosms. The mesocosms were subjected to different conditions that might be observed in actual ponds to completely understand phosphorus dynamics. It is from these results that the variability in phosphorus release is explained.

Altering the dissolved oxygen in the mesocosms led to the development of a relationship with phosphorus release. The sediment oxygen consumption rate was positively correlated with phosphorus release rate. The highest phosphorus release was seen under anoxic conditions. The oxygen consumption in the mesocosms followed the Michaelis-Menten kinetic model, which was used to develop a relation for the maximum oxygen consumption rate and phosphorus release rates. This tool can be used to judge the biological activity of ponds and biologically driven phosphorus release.

Sediment chemical analysis on phosphorus fractions in the sediment was used to develop relationships between loosely bound, iron-bound, labile organic phosphorus, or total phosphorus and release rates. Higher redox sensitive metals in the sediment, like iron, can retain phosphorus under aerobic conditions, but also can release phosphorus during anaerobic conditions. Additionally, labile organic phosphorus can be released when degraded. It was found that both higher iron bound, organic, and total phosphorus concentrations generally correlated with more phosphorus release. The relationships that were developed to relate these bio-chemical pond characteristics to phosphorus release can be used to assess ponds without intensive monitoring. A sample application of

these results is provided for users to predict phosphorus release in ponds without intensive monitoring programs. These tools are meant to act as rough estimates to prioritize maintenance activities, based on results from this research. Additional monitoring may be necessary to fully understand pond dynamics outside of the tools provided.

Several factors, such as spatial variability, influent phosphorus concentration, flushing frequency, and influent particulate concentration, were identified in this study that may have potential impacts on phosphorus release, but more research is needed to fully understand them. Phosphorus release was also shown to vary spatially within a pond, but the hypothesized relationship to inlet and outlet locations varied with each pond and was not uniformly applicable. The effect of influent phosphorous concentration and phosphorus release was examined, but only two different influent phosphorus concentrations were used in the synthetic stormwater flushes, so no clear relationship could be drawn. The effect of storm events on phosphorus concentrations in the ponds was only partially understood from this research, as the simulations did not include influent particulate matter nor different frequencies of flushing.

Experiments on more mesocosms from different ponds can reveal information needed to confirm results from this study and determine if they are applicable to a broader spectrum of ponds. Additionally, long term pond monitoring in-situ along with sediment-water flux mesocosms can determine the accuracy in application of the results of this research. This information can then be used to study the control of phosphorus release from ponds and different maintenance activities that can be refined to maximize pond

efficiency in retaining phosphorus.

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Appendix A

Detailed site descriptions

Information in this Appendix includes specific site descriptions for each of the ponds sampled. Ponds A, B, C, and D are known to the cities they are located in as 52, 849W, William Street, and Roseville Covenant Church ponds. Additionally, conductivity and temperature monitoring data for each pond is included in this Appendix.

Pond 52 is located near downtown St. Cloud, MN in the public Eastman Park next to Lake George. Lake George is an impaired water body for excessive nutrients. The pond receives runoff from the park's parking lot, grounds, and nearby streets. The outlet of the pond drains to the nearby Lake George. There are three inlet locations, two on the west side of the pond, and one on the east side. The outlet is an overflow structure on the north perimeter of the pond.

Figure A.1: Sampling locations in pond 52 (pond A)

Sampling locations in pond 52 are located across the main east-west transact in the pond. Sampling location E was found to be a very sandy soil with large gravel pieces, which was different from the rest of the sampling locations. To ensure that there were five replicate cores with similar sediment characteristics, location F was added.

Pond 849W is in the city of Minnetonka, MN in a residential neighborhood. The pond receives runoff from the bordering lawns and streets. A spillway and culvert inlet exists on the east side of the pond from Spring Crest Drive. Storm drains are also located on the south side of the pond from Hanus Road. The outlet is located on the west end of the pond.

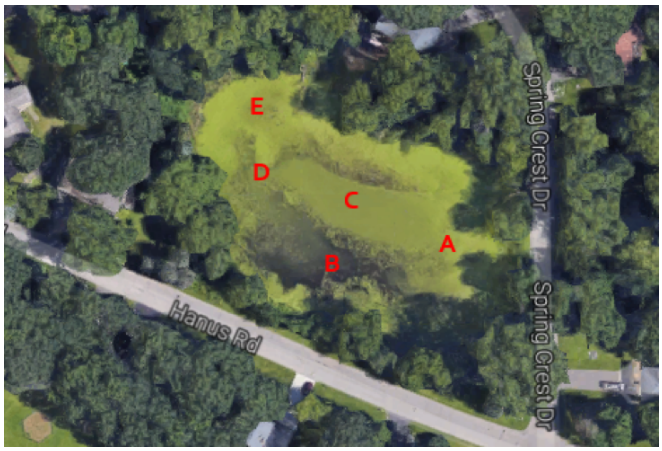

Figure A.2: Sampling locations in pond 849W (pond B)

Most of the sampling locations in pond 849W are located along the preferred flow path of the pond, with location A near the inlet and location E near the outlet. Locations B and C are located in the deepest part of the pond.

William Street Pond is located in Roseville, MN in a residential neighborhood with single family homes and a few apartment complexes. The pond is approximately 1,000 feet north of Lake McCarrons. The inlet for the William Street Pond is located on the north end near Elmer Street. The outlet is located on the southwest end of the pond on William Street North. There is an iron-enhanced sand filter constructed around the perimeter of the pond.

The sampling locations in the William Street pond are located along the main flow path of the pond. Location A is near the inlet of the pond, and location E is near the outlet of the pond. Locations B, C, and D are representative of the middle, deeper parts of the pond.

Roseville Covenant Church pond is located adjacent to the parking lot of Roseville Covenant Church in Roseville, MN. The pond is small and shallow. It has one inlet and one outlet, located on the east and west ends of the pond, respectively.

Though the Roseville Covenant Church pond is small, the sampling locations were chosen to represent any spatial differences in the pond. Location A represents the deepest part of the pond, while locations D and E represent the inlet and outlet, respectively. The sampling depths of each location are very shallow, even in the middle of the pond.

The coordinates of all sampling locations in each pond are given in Figure A.5.

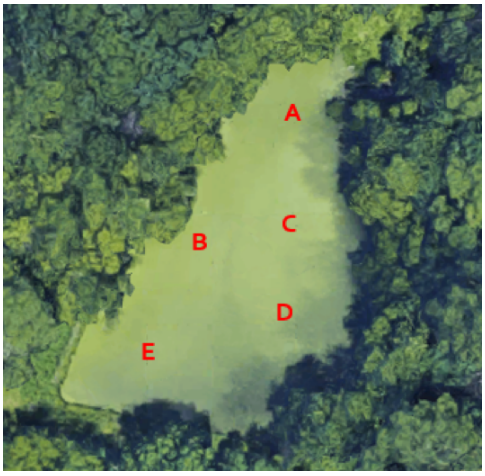

Figure A.3: Sampling locations in William Street pond (pond C)

Figure A.4: Sampling locations in Roseville Covenant Church pond (pond D)

Temperature and conductivity profiles taken in the ponds are given below for ponds A, B, C, and D. Profiles were taken in the middle of each pond, and some profiles were taken near the inlet and outlet in the ponds. These are specified on each figure. These profiles were taken at the same summer season during the year, but 1 year after the cores were sampled.

Figure A.5: Pond sampling location coordinates (Google Maps).

Pond	A	B	C	D	E	F
52 (St. Cloud)	45.554472, -94.162204	45.554525, -94.161963	45.554457, -94.161852	45.554485, -94.161656	45.554543, -94.161586	45.554466, -94.162096
849_W (Minnetonka)	44.901663, -93.514371	44.901617, -93.514868	44.901808, -93.514777	44.901880, -93.515143	44.902037, -93.515099	
William Street (Roseville)	45.001857, -93.110350	45.001674, -93.110538	45.001712, -93.110339	45.001549, -93.110331	45.001484, -93.110703	
Roseville Covenant Church (Roseville)	45.027241, -93.160130	45.027281, -93.160198	45.027280, -93.160093	45.027212, -93.160076	45.027203, -93.160160	

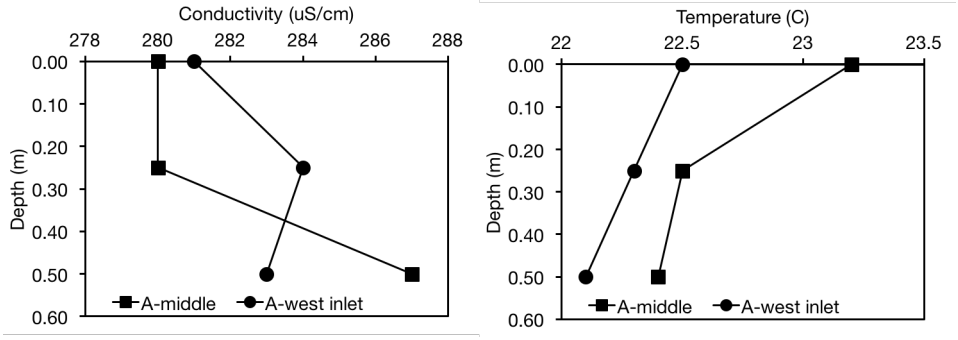

Figure A.6: Conductivity and temperature profiles in pond A

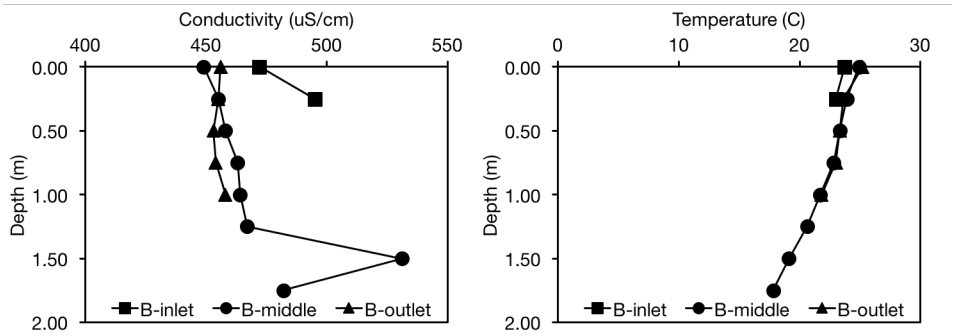

Figure A.7: Conductivity and temperature profiles in pond B

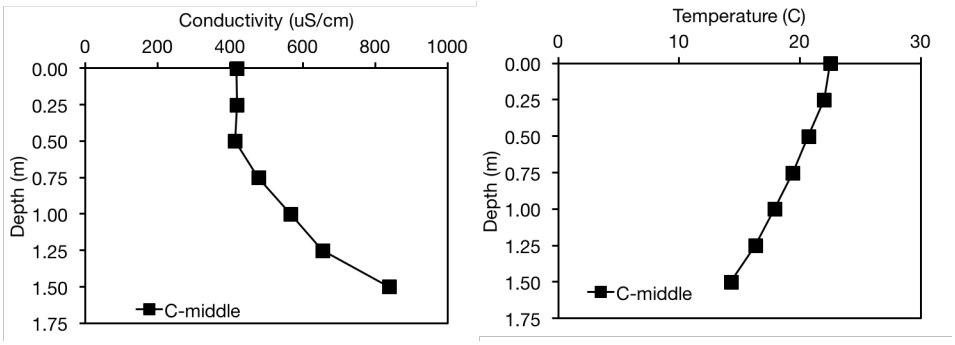

Figure A.8: Conductivity and temperature profiles in pond C

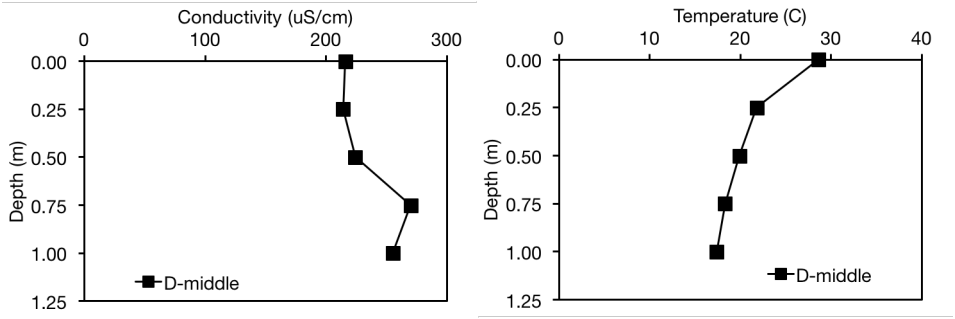

Figure A.9: Conductivity and temperature profiles in pond D

Appendix B

Monitoring Data

This appendix includes the phosphorus (orthophosphate) monitoring data for each mesocosm in the three phases. The first phase for all mesocosms consists of two sets of data: one where orthophosphate was measured 8 cm above the sediment surface and one where orthophosphate was measured halfway up the water column from the sediment surface. The second and third phases only have one set of orthophosphate time-series data, as the water column was completely mixed. The orthophosphate concentration is shown over time in each figure. Each measurement was used to calculate the mass of phosphorus in the water column using methods outlined in Section 3. The data was truncated at 14-days for the flux calculations, but the rest of the monitoring data is included here. At the end of this appendix, pH data over time is given.

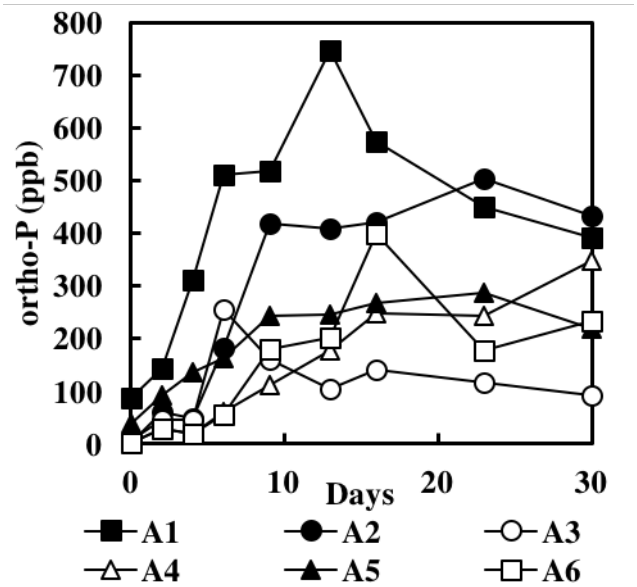

Figure B.1: Phosphorus concentration change over time in phase 1 at 8 cm above the sediment surface, pond A

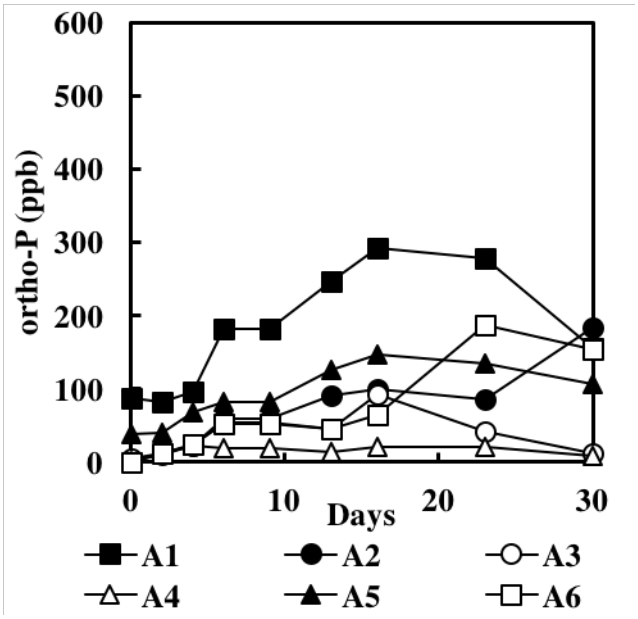

Figure B.2: Phosphorus concentration change change over time in phase 1 at the mid-point of the water column, pond A

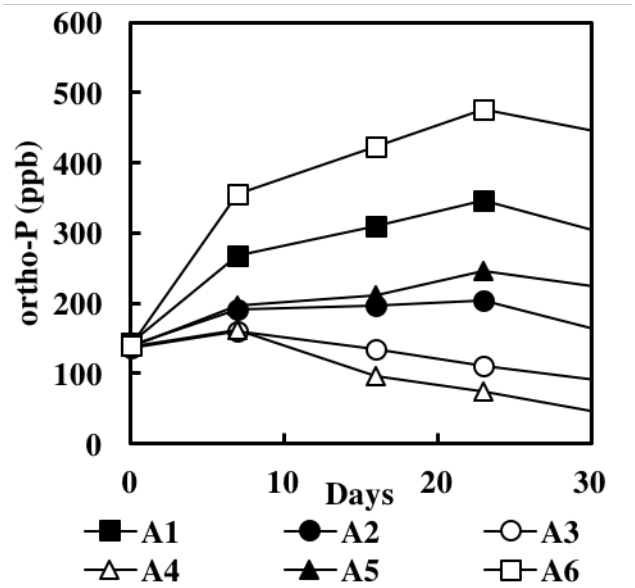

Figure B.3: Phosphorus concentration change over time in phase 2, pond A

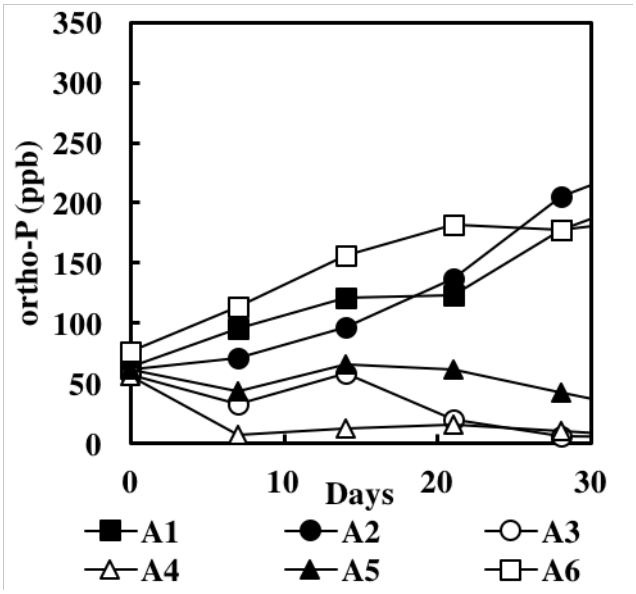

Figure B.4: Phosphorus concentration change over time in phase 3, pond A

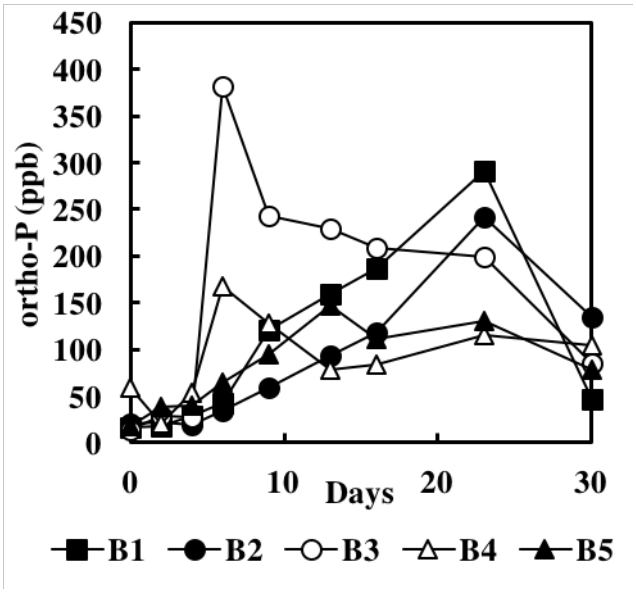

Figure B.5: Phosphorus concentration change over time in phase 1 at 8 cm above the sediment surface, pond B

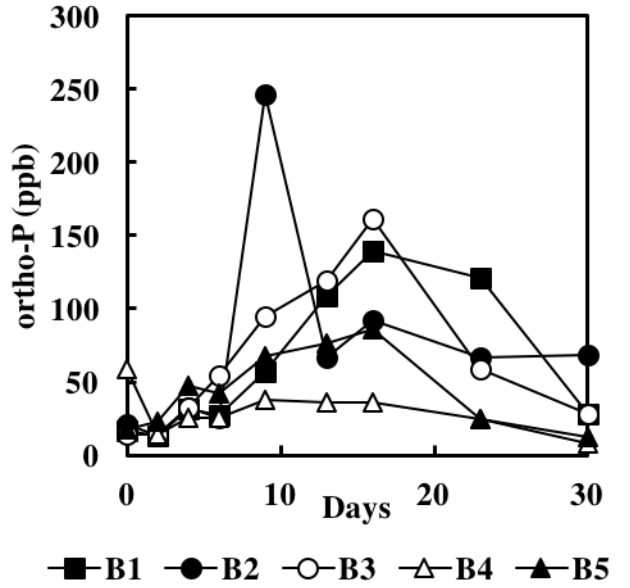

Figure B.6: Phosphorus concentration change over time in phase 1 at the midpoint of the water column, pond B

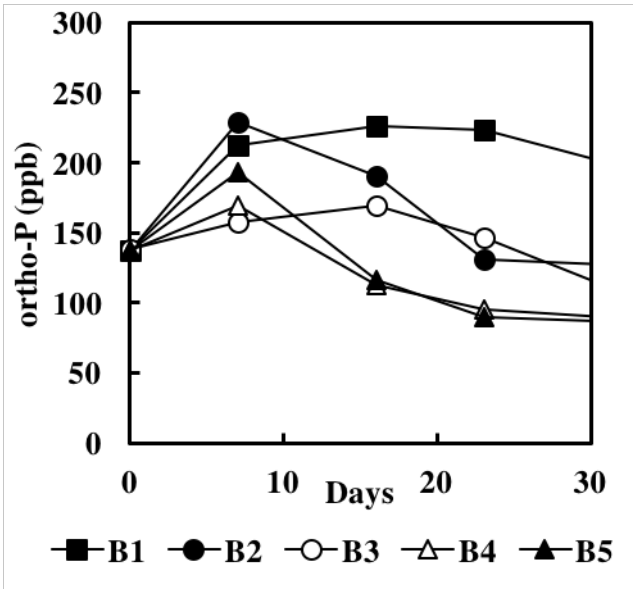

Figure B.7: Phosphorus concentration change over time in phase 2, pond B

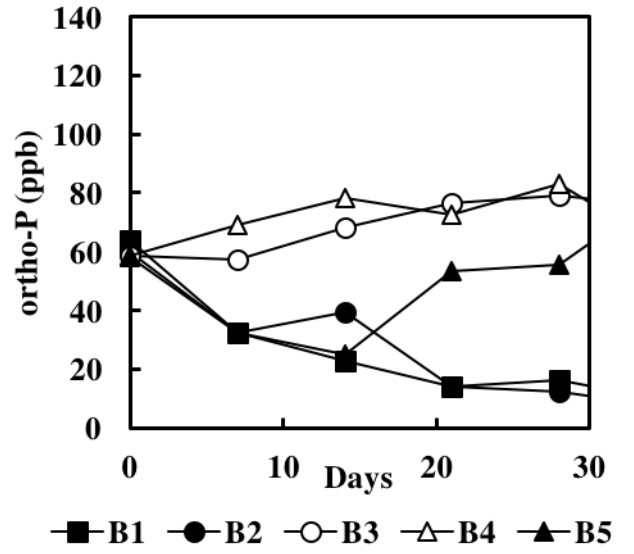

Figure B.8: Phosphorus concentration change over time in phase 3, pond B

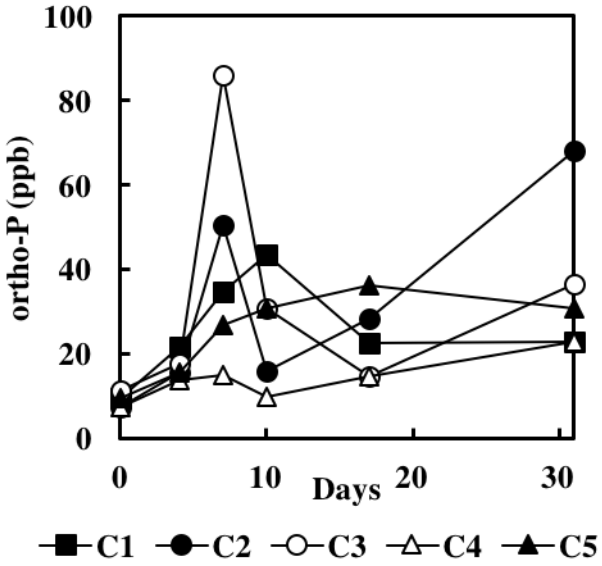

Figure B.9: Phosphorus concentration change over time in phase 1 at 8 cm above the sediment surface, pond C

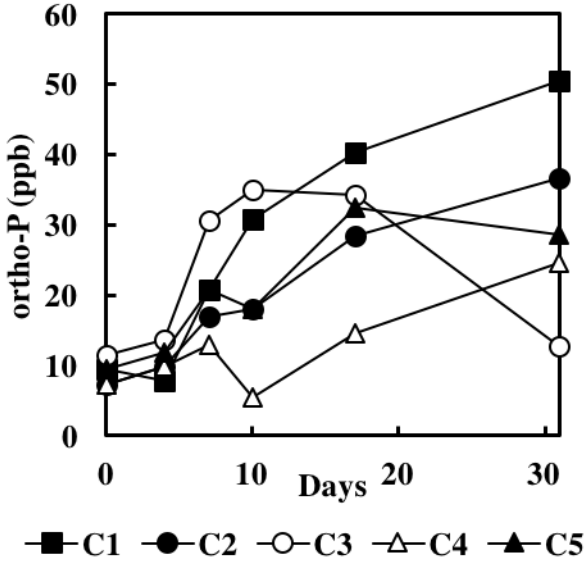

Figure B.10: Phosphorus concentration change over time in phase 1 at the midpoint of the water column, pond C

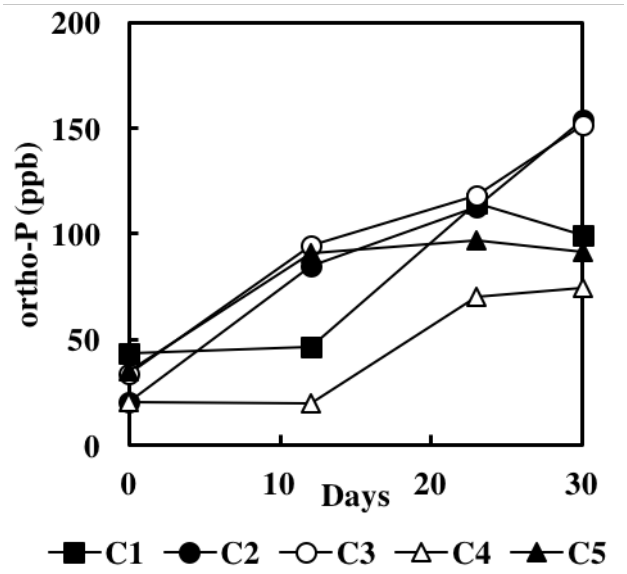

Figure B.11: Phosphorus concentration change over time in phase 2, pond C

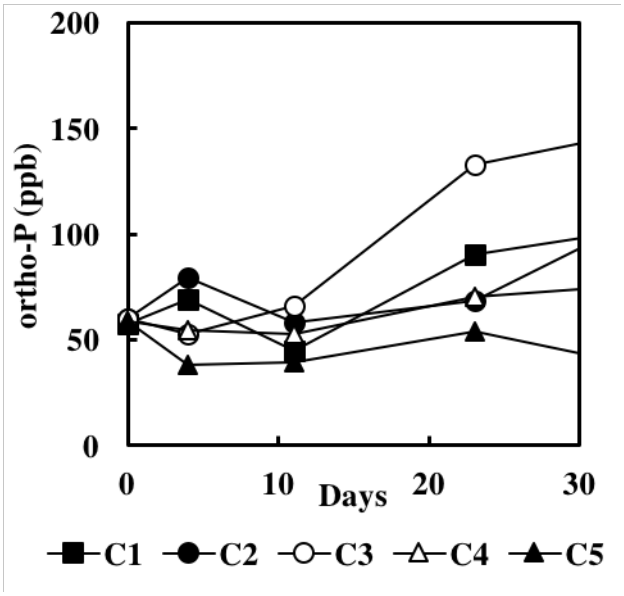

Figure B.12: Phosphorus concentration change over time in phase 3, pond C

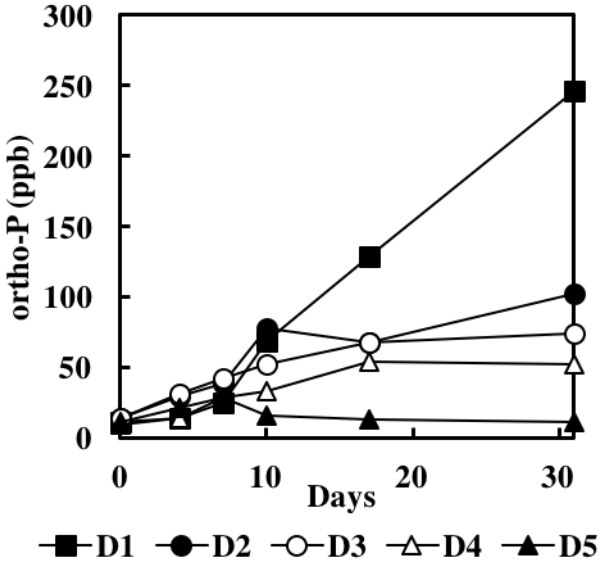

Figure B.13: Phosphorus concentration change over time in phase 1 at 8 cm above the sediment surface, pond D

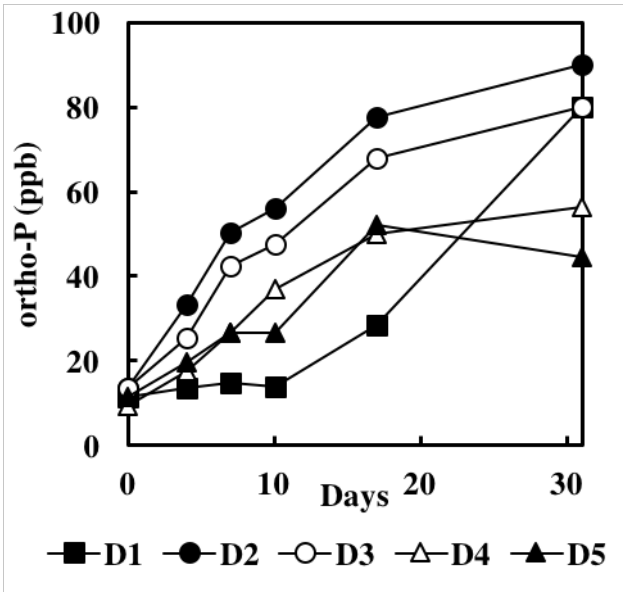

Figure B.14: Phosphorus concentration change over time in phase 1 at the midpoint of the water column, pond D

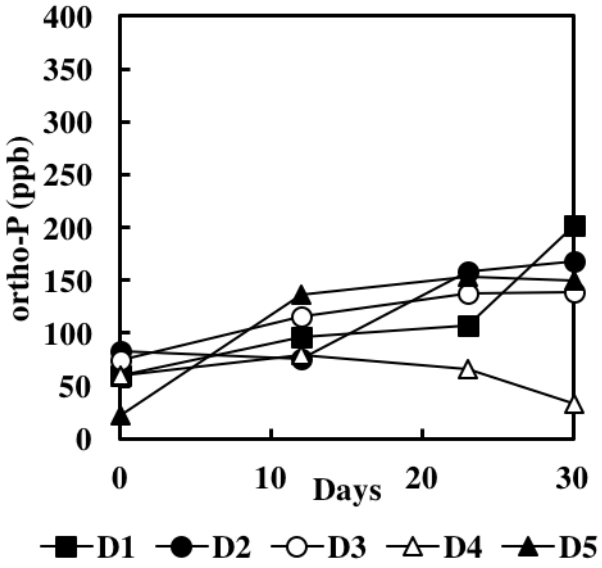

Figure B.15: Phosphorus concentration change over time in phase 2, pond D

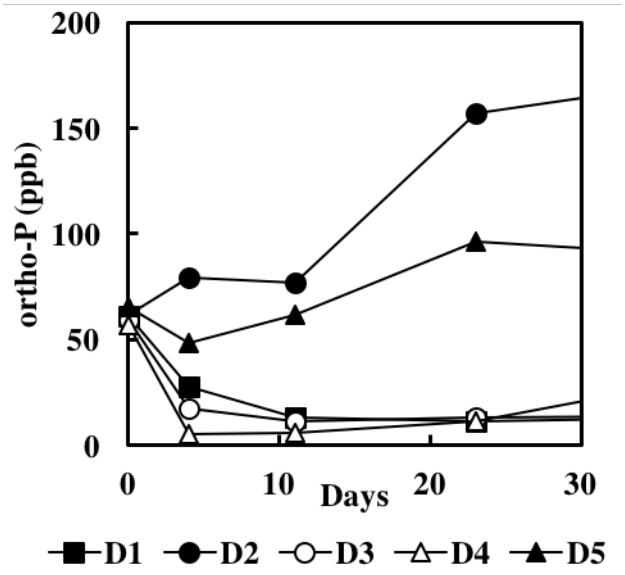

Figure B.16: Phosphorus concentration change over time in phase 3, pond D

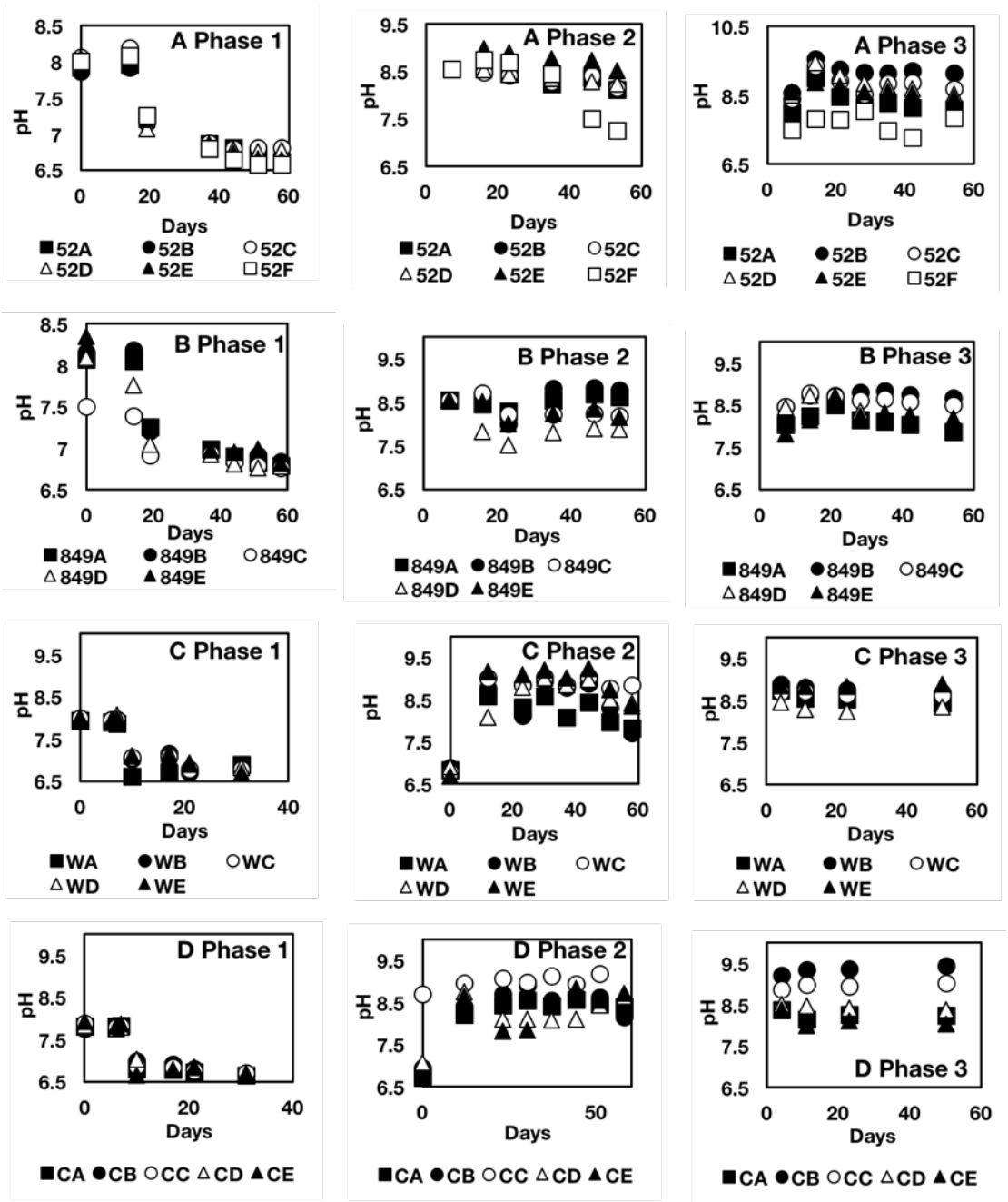

Figure B.17: pH change over time in each phase for all ponds

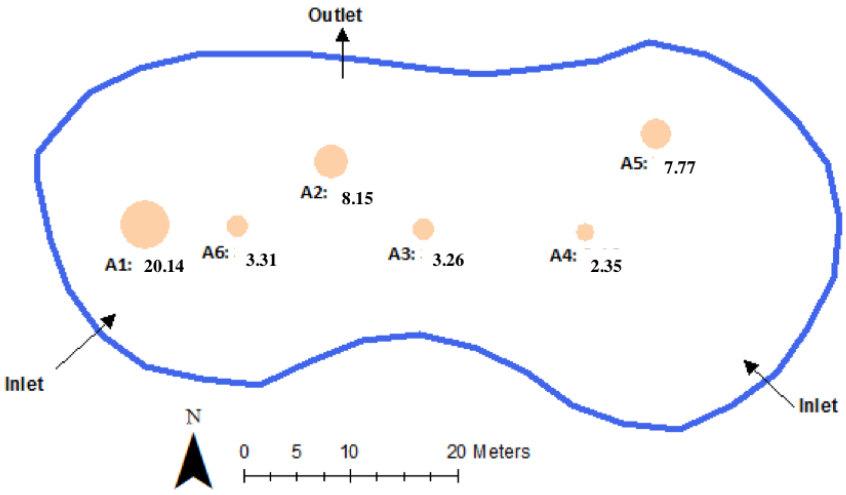

Figure B.18: Spatial phosphorus flux in pond A from phase 1

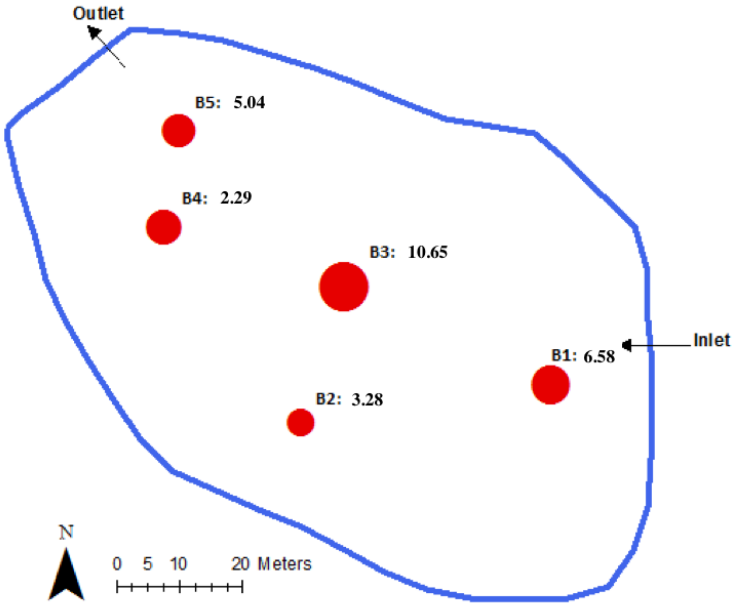

Figure B.19: Spatial phosphorus flux in pond B from phase 1

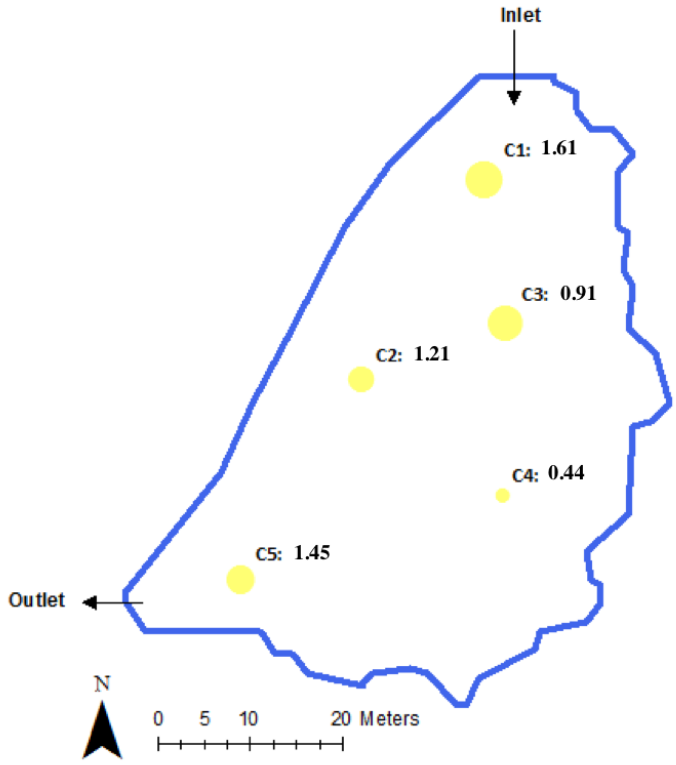

Figure B.20: Spatial phosphorus flux in pond C from phase 1

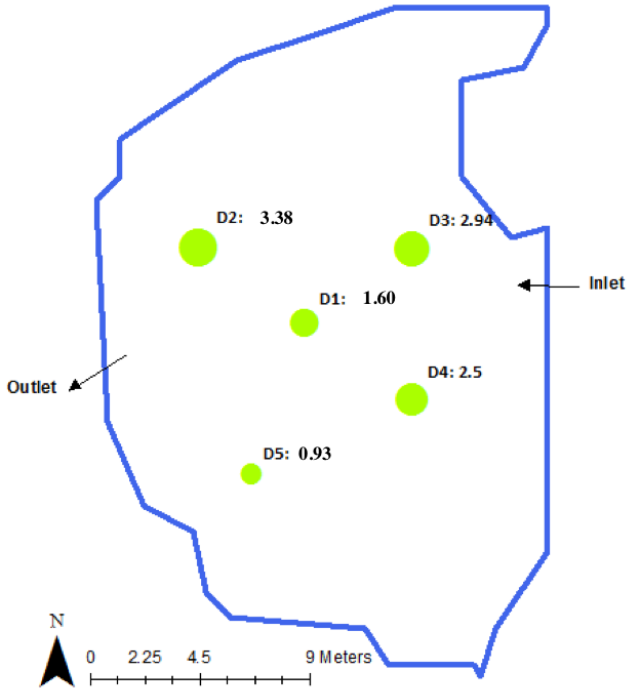

Figure B.21: Spatial phosphorus flux in pond D from phase 1

Appendix C

Sediment Data

The sediment analysis consisted of extracting different forms of bound phosphorus in 1 cm and 3 cm intervals in the sediment cores of the mesocosms. The water content and organic matter content values are given in Figures C.1 through C.8. The different phosphorus fractions are given as profiles of magnitude versus depth for each mesocosm in Figures C.9 through Figure C.23. The phosphorus concentrations are given as mg/kg based on dry weight.

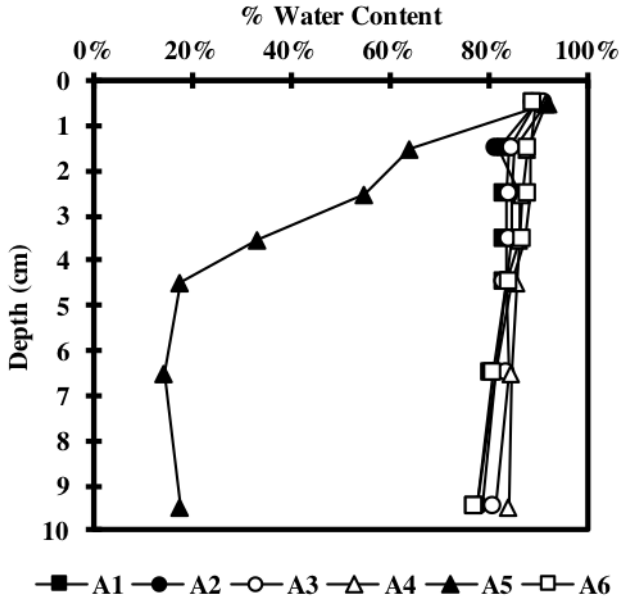

Figure C.1: Water content in pond A mesocosms

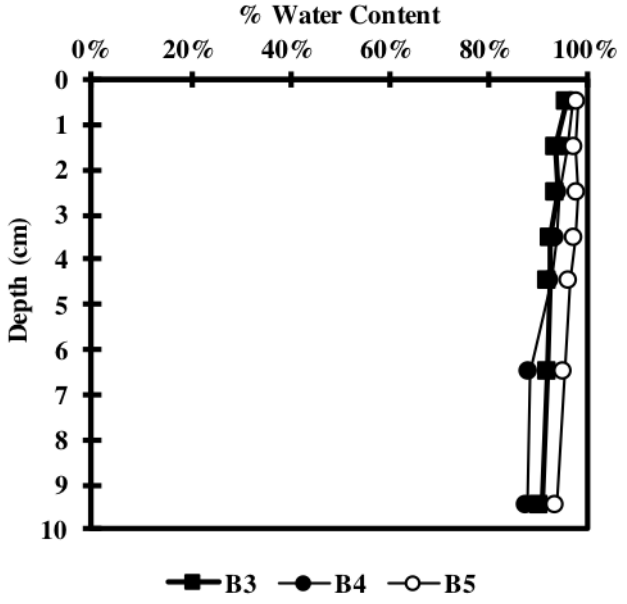

Figure C.2: Water content in pond B mesocosms

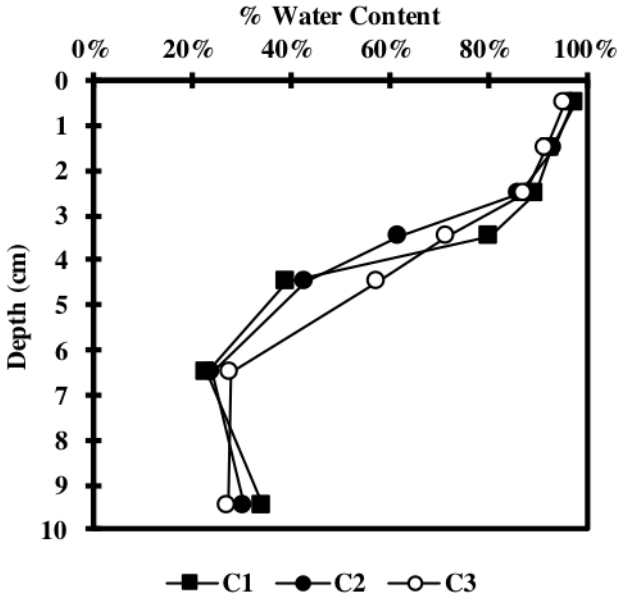

Figure C.3: Water content in pond C mesocosms

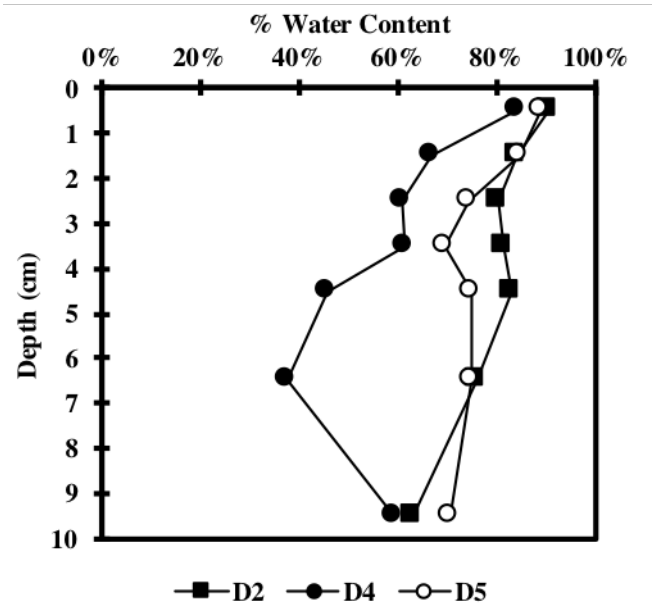

Figure C.4: Water content in pond D mesocosms

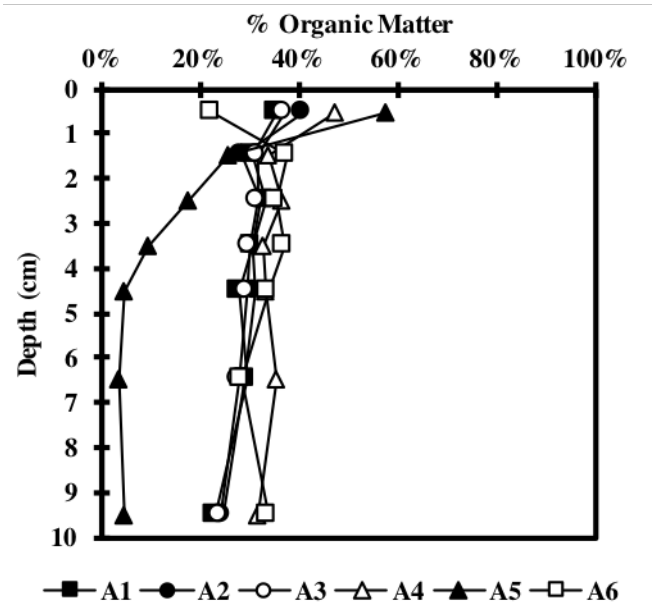

Figure C.5: Organic matter content in pond A mesocosms

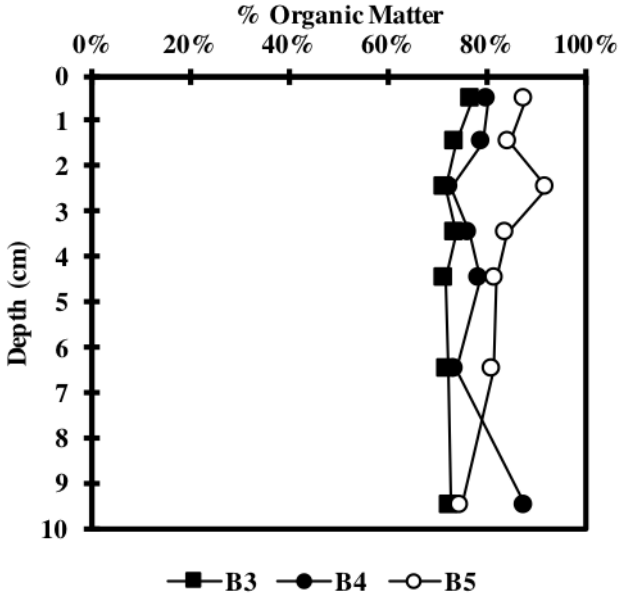

Figure C.6: Organic matter content in pond B mesocosms

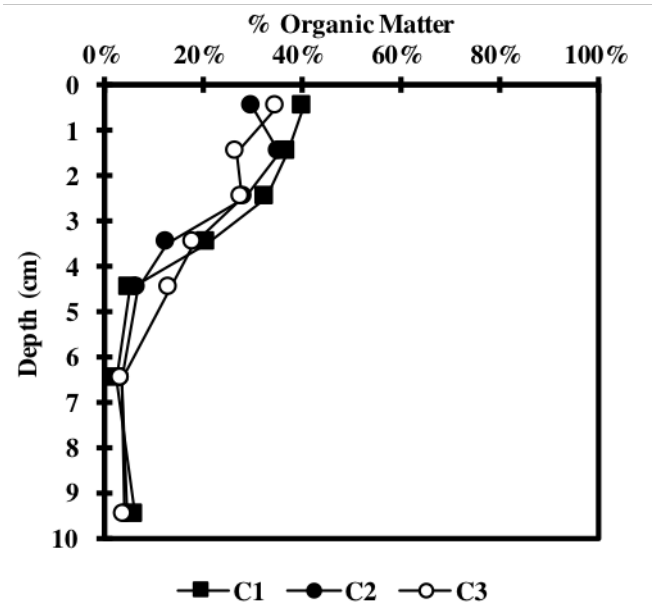

Figure C.7: Organic matter content in pond C mesocosms

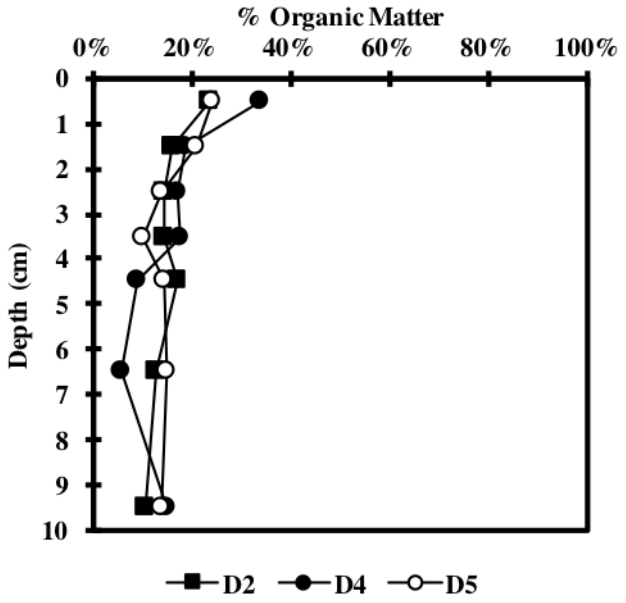

Figure C.8: Organic matter content in pond D mesocosms

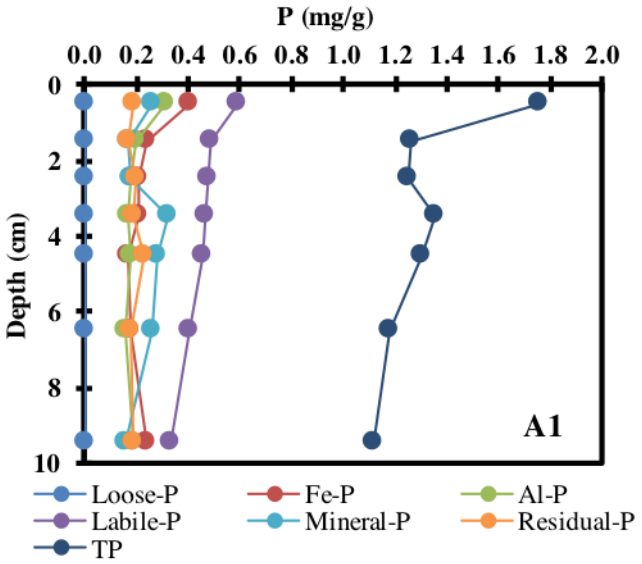

Figure C.9: Sediment phosphorus fraction profiles in mesocosm A1

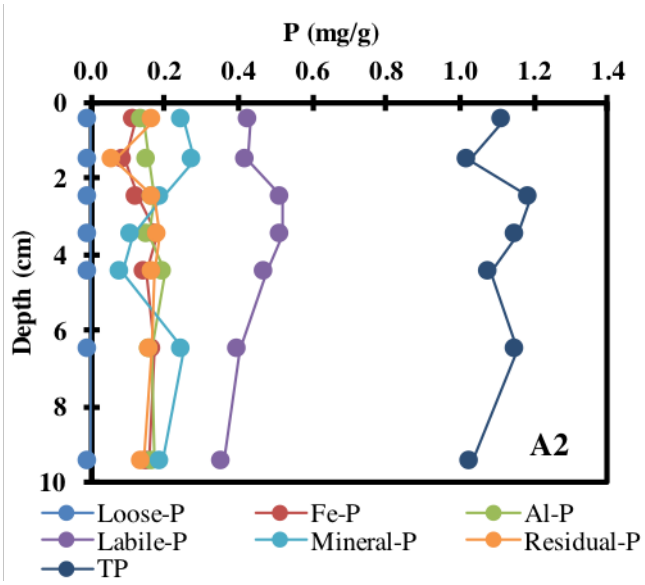

Figure C.10: Sediment phosphorus fraction profiles in mesocosm A2

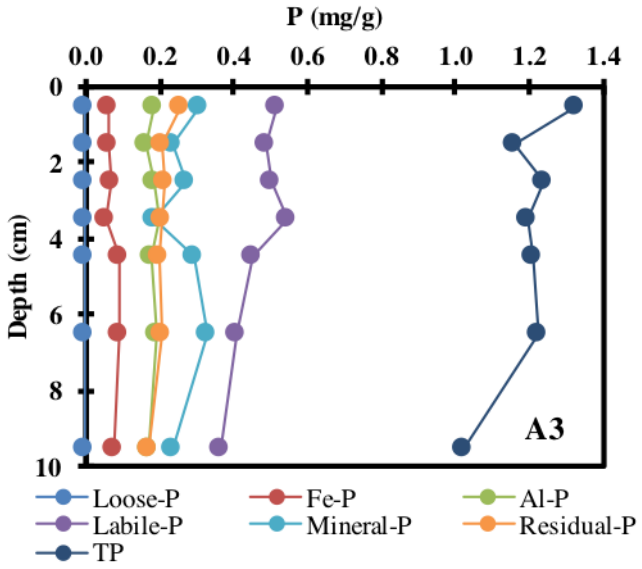

Figure C.11: Sediment phosphorus fraction profiles in mesocosm A3

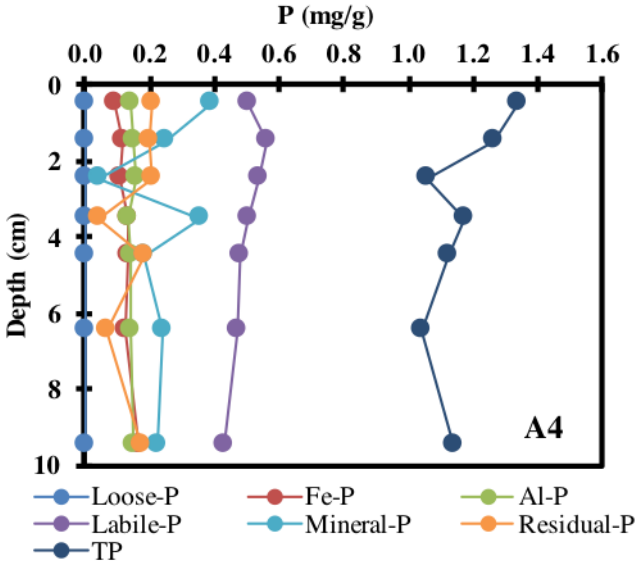

Figure C.12: Sediment phosphorus fraction profiles in mesocosm A4

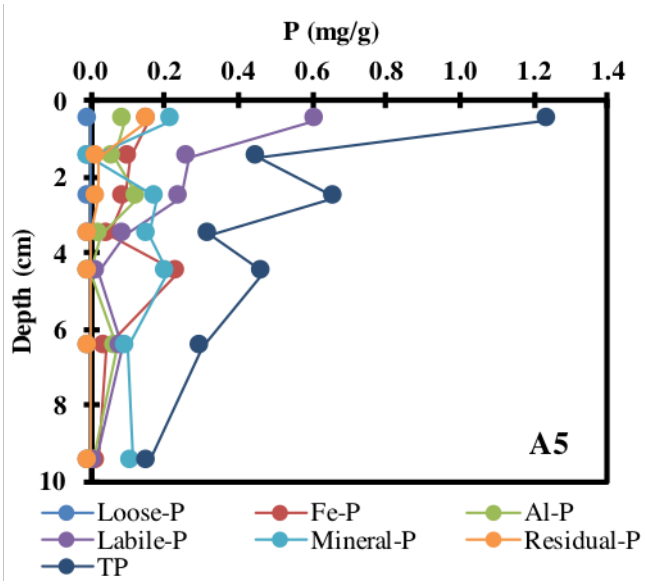

Figure C.13: Sediment phosphorus fraction profiles in mesocosm A5

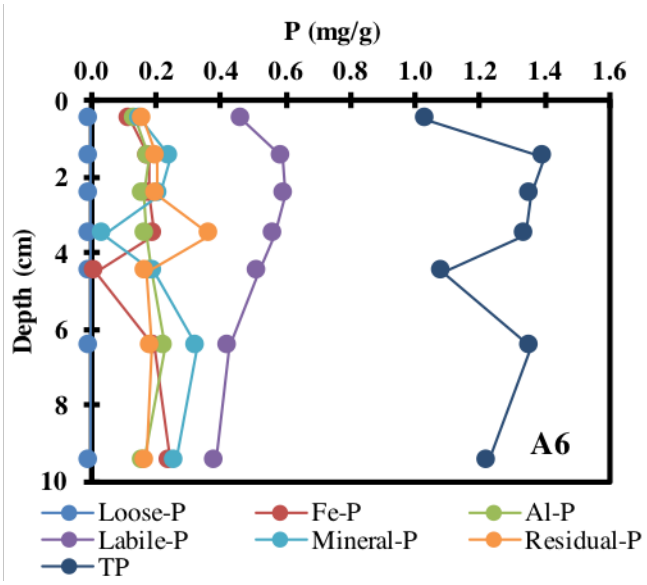

Figure C.14: Sediment phosphorus fraction profiles in mesocosm A6

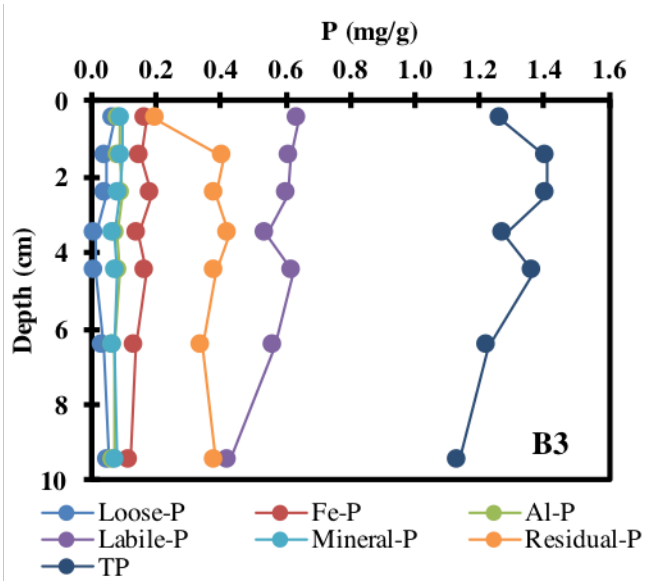

Figure C.15: Sediment phosphorus fraction profiles in mesocosm B3

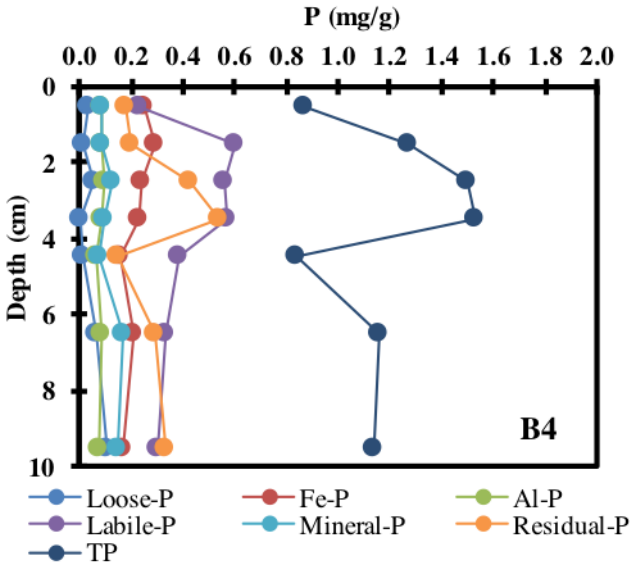

Figure C.16: Sediment phosphorus fraction profiles in mesocosm B4

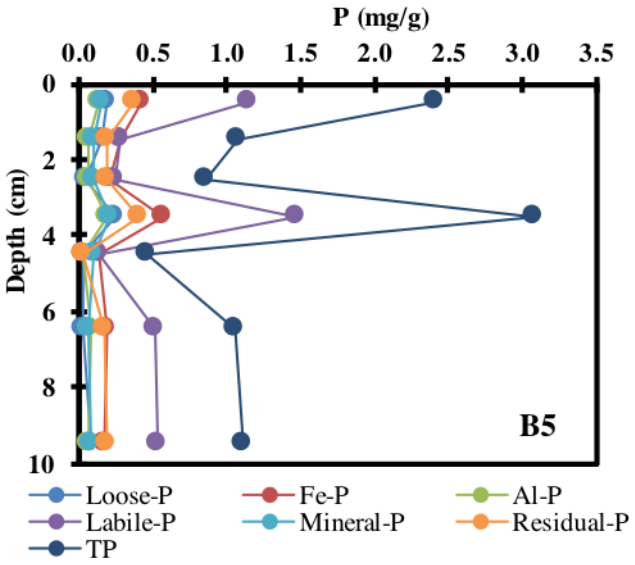

Figure C.17: Sediment phosphorus fraction profiles in mesocosm B5

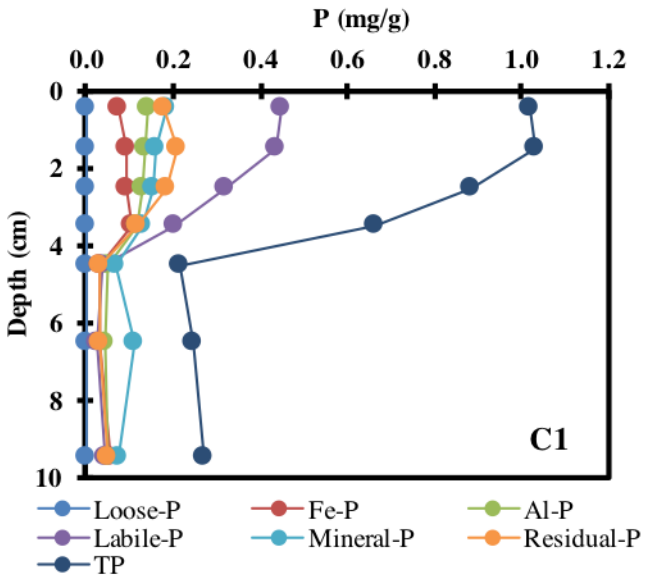

Figure C.18: Sediment phosphorus fraction profiles in mesocosm C1

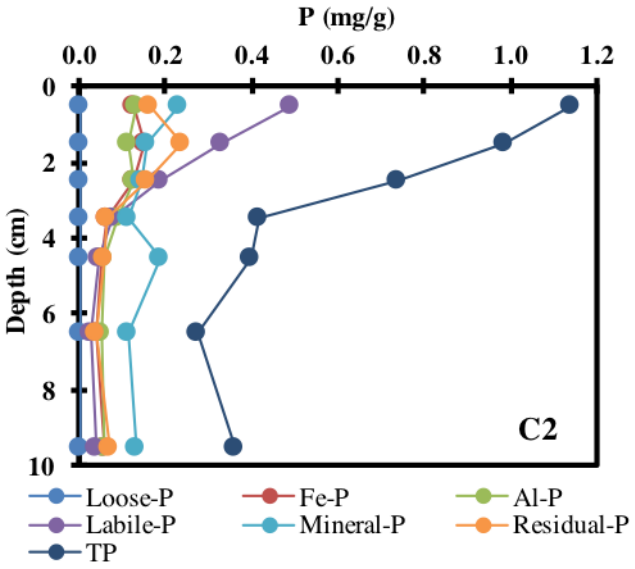

Figure C.19: Sediment phosphorus fraction profiles in mesocosm C2

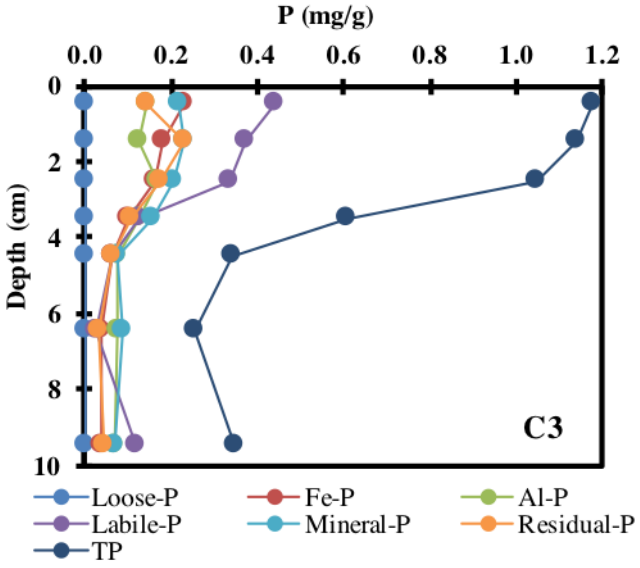

Figure C.20: Sediment phosphorus fraction profiles in mesocosm C3

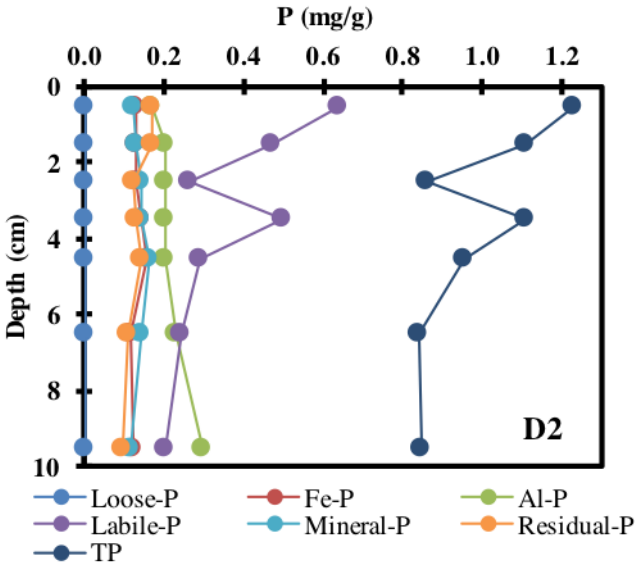

Figure C.21: Sediment phosphorus fraction profiles in mesocosm D2

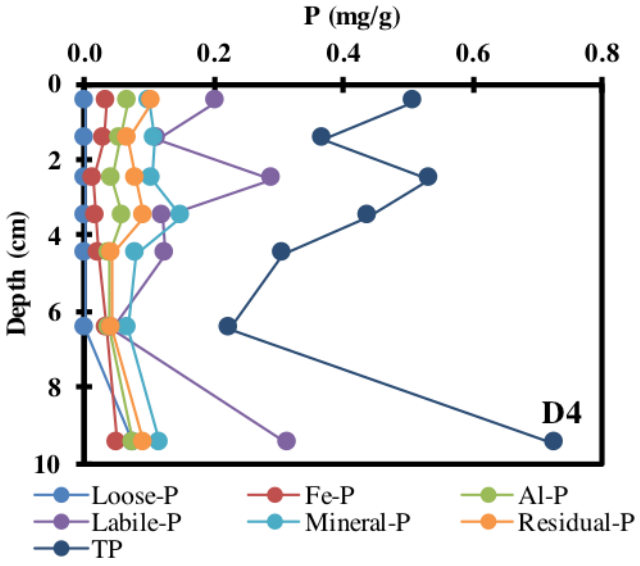

Figure C.22: Sediment phosphorus fraction profiles in mesocosm D4

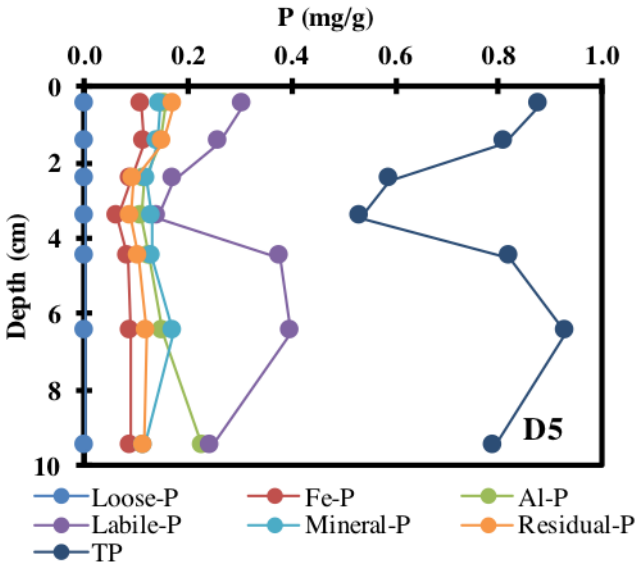

Figure C.23: Sediment phosphorus fraction profiles in mesocosm D5